SEA WATER CONVERSION LABORATORY

UNIVERSITY OF CALIFORNIA

BERKELEY, CALIFORNIA

"Study of Permeability Characteristics of Membranes"

Combined Quarterly Reports Nos. 15 and 16

January 15, 1972

K. S. Spiegler, Principal Investigator
R. J. Moore
J. Leibovitz (part-time)
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Contract No. 952109
Jet Propulsion Laboratory
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ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

The purpose of combining two Quarterly Progress Reports under one cover is twofold; first,the breadth of the topic treated here (viz. bridging the gap between theory and experiment) is such that the task was not completed at the end of the first quarter, and breaking the results into two parts would only have caused unnecessary detouring of the readers' effort; second, the degree of work intensity was less than before since some staff was on summer vacation during the first quarter, while a portion of the second quarter was in the period of the no-cost extension of this contract, when one of the investigators (Mr. Messalem) had left for another appointment. It is of interest that in spite of these factors, the progress achieved in the last two quarters seems to us of decisive importance.

A method of evaluation of the transport experiments was worked out which is based entirely on conservative fluxes, i.e. fluxes of quantities which do not vary across the membrane in the steady state (the "volume flux" and "separation flux" which have been used frequently in the past by other investigators are not conservative). Using this procedure the conductance coefficients for the system

0.05 N NaCl | C-103 cation-exchange membrane* | 0.1 N NaCl

were calculated. In these calculations two reciprocity relations (one relating to salt flow - water flow coupling in osmosis and hyperfiltration $L_{sw} = L_{ws}$, the other relating membrane potential to cation transference number $L_{se} = L_{es}$) were <u>assumed</u> to be satisfied; the third (relating streaming

*American Machine & Foundry Co., Stamford, Connecticut.

potential to electroosmosis, $L_{ew} = L_{we}$) was proven to hold within 6 percent, at least up to a pressure difference of one atmosphere. In the future it should be possible to obtain sufficiently accurate membrane potential measurements to determine the range of validity of the reciprocity relation $L_{se} = L_{es}$. We do not expect to be able to verify the reciprocity relation $L_{sw} = L_{ws}$ in our apparatus, since the pressures necessary to determine the hyperfiltration coefficient, L_{ws}, with reasonable accuracy are higher than our apparatus can support.*

The calculation of the conductance coefficients, L, which characterize the transport properties of the membrane, was performed with the experimental data available from recent and earlier experiments. Not all of these data were of the high accuracy which we can now achieve; moreover some of the data came from experiments in which the membrane was in contact with 0.1 N NaCl solutions on both sides, rather than 0.1 N on one and 0.05 N on the other; but several importants points emerge from consideration of the calculated L-values (Table 4) and the methods used to calculate these values; viz. (a) The coefficients related to a larger extent to water, w, than to salt, s, are larger ($L_{ew} >> L_{es}$; $L_{ww} >> L_{ws}$; $L_{sw} >> L_{ss}$; subscript e stands for the electric current). This is probably due to the much higher concentration of water than of salt in the ion-exchange membrane, for the coefficients L_{ij} increase in general with increasing c_j. This property of the set of L-coefficients thus probably reflects the exclusion of salt from the ion-exchange membrane ("Donnan effect").

*This limitation was known since the principal investigator's early high-pressure hyperfiltration experiments performed in steel vessels (1). The advantages of a plastic cell for the concentration-clamp apparatus seemed so large, however, that it was decided at the start of this research to forego the determination of the validity range of the reciprocity relation $L_{ws} = L_{sw}$; the other two reciprocity relationships can be checked in our concentration-clamp apparatus.

(b) The numerical calculations in section A. 2. of the Appendix show the large dependence of all L-coefficients on the membrane conductance. In fact, membrane conductance emerges as the most decisive transport characteristic, thus justifying a posteriori the time-honored decision of battery technologists to use conductance measurements as primary screening tests for separator materials. The implication of this conclusion for future experiments is the emphasis on refinements of the technique of membrane conductance measurements. A more elaborate and more accurate technique than the one used in the past is being developed. It uses the existing apparatus described in Progress Report No. 12. Apparatus and procedure were modified to yield much more accurate measurements of the distances of the electrodes from the membrane. (c) Consideration of the numerical values of all terms in the calculation of the conductance parameter, L_{ss}, which relates the rate of electrolyte diffusion through the membrane to the "electrolyte diffusion force", $-\Delta\mu_s$, (determined by the concentration gradient of the electrolyte) leads one to the conclusion that osmosis $\leftrightarrow$ dialysis with shorted electrodes (rather than with unconnected electrodes) should be tried, in an attempt to improve the accuracy of this determination. Also it would be worthwhile to investigate under what conditions, if any, the planned, simultaneous application of several independent forces improves the accuracy of the determination of the conductance coefficients, L.

Finally, the methods developed here for calculating a set of L-coefficients from specified transport measurements lead to the unequivocal characterization of any system of the type: solution | membrane | solution

provided only that these specified measurements can be performed with sufficient accuracy. The "concentration-clamp" apparatus developed in this project represents a large step towards the attainment of this experimental aim.

In the future we propose to (A) measure those transport coefficients (e.g. electrical conductance) for the system

0.05 N NaCl | C-103 | 0.1 N NaCl

which we had previously measured only for the system

0.1 N NaCl | C-103 | 0.1 N NaCl,

(B) use the method described in this report for systematic studies of other solution-membrane systems and (C) investigate the points mentioned under (c) above.

LIST OF SYMBOLS

A	effective surface area of membrane, cm^2
c	concentration, mole cm^{-3}
$\bar{c}$	average between left and right concentrations, mole cm^{-3}
d	membrane thickness, cm
F	generalized force (e.g. $\Delta\tilde{\mu}$), joule $mole^{-1}$
i	electric current density, amp cm^{-2}
J_i	flux of component i, mole cm^{-2} sec^{-1}
J_D	"separation flux" defined in eq. (14), mole cm^{-2} sec^{-1}
J_V	volume flux, cm sec^{-1}
L_{ij}	conductance coefficient in "Onsager set of transport equations" (3)-(5). i, j = +, -, w; $mole^2$ $joule^{-1}$ cm^{-2} sec^{-1}
L_{VV}, L_{DD}, L_{EE}, etc.	conductance coefficients in "Duncan set of transport equations" (23)-(25). For units, see Table 1
L_{ss}, L_{ww}, L_{ee}, etc.	conductance coefficients in "Michaeli-Kedem set of transport equations" (35)-(37), $mole^2$ $joule^{-1}$ cm^{-2} sec^{-1}
p	pressure, dekabar*
R	gas constant, 8.31 joule $mole^{-1}$ $(^oK)^{-1}$
T	temperature, ^oK
t	time, sec
t_i	transference number of component i, relative to the membrane
$\bar{v}_i$	partial molar volume of component i, mole cm^{-3}
v_{Cl}	$\equiv \bar{v}_{AgCl} - \bar{v}_{Ag}$ [eq. (A1-13)], cm^3 $mole^{-1}$
z_i	valency of particle i, equiv $mole^{-1}$ (positive for cations, negative for anions, zero for water)
$\mathfrak{F}$	Faraday's constant, 0.965×10^5 coul eq^{-1}
$\Delta\phi$	electric potential difference across membrane, volt**

* 1 dekabar = 1 joule cm^{-3} = 10 bar = 9.8692 atm.

** often measured with "Luggin capillaries".

$\Delta\phi_-$	potential difference between two Ag/AgCl (anion-reversible) electrodes in solutions adjacent to membrane, volt
κ	conductivity, $ohm^{-1}\ cm^{-1}$
ρ	resistivity, ohm cm
$\tilde{\mu}_i$	total potential of component i [eq. (26)], joule $mole^{-1}$
μ_i	chemical potential of component i (includes pressure-volume term), joule $mole^{-1}$
μ_i^c	concentration-dependent part of chemical potential of component i, joule $mole^{-1}$

Subscripts

+	cation
-	anion (Cl^- in this report)
w	water
s	electrolyte (NaCl in this report). The equations refer to an electrolyte composed of a cation of valency +1 and an anion of valency -1 ("1-1" electrolyte)

Sign Conventions

(1) Positive direction is from left to right. (2) Fluxes from left to right are counted positive. (3) The operator, Δ, for finite differences refers to the value on the right (double primes) minus the value on the left (single primes), as does conventionally the differential operator, d.

Driving forces are of the general form $(-d\tilde{\mu}/dz)$. Thus positive values of the driving force, $(-d\tilde{\mu}/dz) > 0$, lead to positive fluxes. For example, Ohm's law is

$$i = (1/\rho) \underbrace{\left(-\Delta\phi \right)}_{\text{"Driving force"}}$$

and Fick's law

$$J_i = D_i \underbrace{\left(-\Delta c_i \right)}_{\text{"Driving force"}}$$

THEORY

We consider the isothermal system

Ag/AgCl | chloride solution, c' | membrane | chloride solution, c" | Ag/AgCl

There are three types of particles which can migrate in the membrane, viz. cations (+), Cl^- (-) and water (w). Three equations relating the fluxes, J (mole cm^{-2} sec^{-1}) to the generalized forces, F (wattsec $mole^{-1}$) are necessary to characterize the transport properties of the system.

The most fundamental set of transport equations is based on the classical concepts of non-equilibrium thermodynamics (2) originally developed by Onsager (3) and applied by him to diffusion in liquids (4). Previous experimental work justifies the description of the fluxes as sums of the products of generalized forces and conductance coefficients, L_{ij}:

$$J_i = \sum_j L_{ij} F_j \qquad (1)$$

From a practical viewpoint it is essential to look for transport descriptions with reasonably constant conductance coefficients (i.e. conductance coefficients which are reasonably independent of the forces). Only in this case does a single set of L_{ij} coefficients characterize a given membrane-solution system, i.e. enable us to predict the fluxes from knowledge of the forces and/or vice-versa.

For ion and water transport in membranes under the influence of differences of pressure, concentration and/or electric potential, the generalized force acting on particle i is

$$F_i = \bar{v}_i \Delta p + \Delta \mu_i^c + z_i \mathfrak{F} \Delta \phi \qquad (2)$$

where Δp (dekabar*), $\Delta\mu_i^c$ (wattsec mole^{-1}) and $\Delta\phi$ (volt) are the differences of pressure, of the "concentration-dependent part of the chemical potential" $\left[\text{i.e. } \left(\frac{\partial\mu_i}{\partial c_i}\right)\Delta c_i = RT\Delta\ln a_i\right]$ and the electrical potential across the membrane respectively. Hence the original set of transport equations (which we shall call the "Onsager set") is

$$J_+ = - L_{+w}(\bar{v}_w\Delta p + \Delta\mu_w^c) - L_{++}(\bar{v}_+\Delta p + \Delta\mu_+^c + \mathcal{F}\Delta\phi) - L_{+-}(\bar{v}_-\Delta p + \Delta\mu_-^c - \mathcal{F}\Delta\phi) \qquad (3)$$

$$J_- = - L_{-w}(\bar{v}_w\Delta p + \Delta\mu_w^c) - L_{-+}(\bar{v}_+\Delta p + \Delta\mu_+^c + \mathcal{F}\Delta\phi) - L_{--}(\bar{v}_-\Delta p + \Delta\mu_-^c - \mathcal{F}\Delta\phi) \qquad (4)$$

$$J_w = - L_{ww}(\bar{v}_w\Delta p + \Delta\mu_w^c) - L_{w+}(\bar{v}_+\Delta p + \Delta\mu_+^c + \mathcal{F}\Delta\phi) - L_{w-}(\bar{v}_-\Delta p + \Delta\mu_-^c - \mathcal{F}\Delta\phi) \qquad (5)$$

Onsager's theoretical work (3) based on statistical mechanics led to the conclusion that the conductance coefficients, L_{ij}, satisfy the reciprocity condition

$$L_{ij} = L_{ji} \qquad (6)$$

Onsager's work is of general nature and covers many more phenomena than transport in membranes, e.g. heat conduction and chemical reactions. In general, the range of validity of linear laws of the type of eq. (1) is limited; for instance for most chemical reactions the linear approximation is reasonably adequate only very close to chemical equilibrium. If this were generally true for transport in membranes also, the linear equations would therefore be only of very limited use; for many transport phenomena, however, the range of approximate linearity extends far beyond equilibrium. For instance, it has been known for many decades that the ion flux in electrolyte solutions is proportional to the applied electric voltage over a considerable

*1 dekabar ≡ 10 bar ≃ 9.87 atm; this pressure unit is used in order to minimize the use of conversion factors in our system of units (see List of Symbols).

voltage range, provided proper electrodes and stirring devices are used ("Kohlrausch's law"). Also self-diffusion of particles follows a strictly linear relationship between flux and force even in solutions and gases which are very far from isotopic equilibrium [Fick's law of diffusion can be shown to be a linear law in the sense of eq. (1); see, for instance refs. (5) and (6)]. Moreover, many membranes and porous media satisfy d'Arcy's law (proportionality between water flux and pressure difference, Δp) up to quite high values of Δp. Therefore the range of applicability of the linear transport equations (3) - (5) might prove to be appreciable, at least with respect to variations of pressure, Δp and electrical potential differences, $\Delta\phi$ (7). As for $\Delta\mu^c$, the situation is more complex. There are membranes in which some conductance coefficients are only mildly affected by changes in the concentrations of the solutions bracketing the membrane. For instance, present knowledge on the nature of ion-exchange membranes leads one to believe that changes in the concentrations of dilute solutions (up to about 0.5 N NaCl) should only very moderately change the cation conductance coefficient, L_{++} in high-capacity cation-exchange membranes (such as C-103 used here), since the "Donnan-effect" excludes the anions from the membrane to a large extent. On the other hand, a relatively much larger change of the anion transport coefficient, L_{--}, with the concentration of the bracketing solutions is expected; this coefficient varies very strongly with the concentration, $\bar{c}_-$, of the anions in the membrane (8, eq. 17), and, while of small magnitude, percentage-wise $\bar{c}_-$ varies considerably with the concentrations of the bracketing solutions.

In other words, the electrical conductivities of these membranes when equilibrated with pure water and 0.1 N NaCl vary only by a few percent since in both cases the electric current is carried primarily by cations whose concentration in the membrane varies relatively little in the two cases. On the other hand, anion transport and salt diffusion are controlled by the anion concentration distribution in the membrane which varies relatively much in the two cases, being zero for the membrane equilibrated with pure water and small, but finite, for the membrane equilibrated with 0.1 N NaCl (7). In non-permselective membranes, both L_{++} and L_{--} vary strongly with the concentration. Therefore one can not a priori expect constancy of all the conductance coefficients with respect to variations in the solution concentrations. (The "concentration-clamp" method was invented with this thought in mind; it keeps the solution concentrations constant at least while each experiment for the measurement of transport parameters is in progress). Since one is interested in an invariant* set of transport parameters for each system consisting of a given membrane and a preferably wide concentration range of solutions of a given electrolyte, attempts have been made to break down the conductance coefficients into products of concentrations and so-called "friction coefficients" in the hope that the latter vary only mildly with the concentration (8,9). Preliminary results of this type of analysis by many investigators [summarized in ref. (10)] look quite promising; this report does not present this analysis, however, since we don't have enough experimental data on our system yet.

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*i.e. independent of the concentrations and all forces.

The practical application of the Onsager set of transport equations [eqs. (3) - (5)] is hampered by the lack of knowledge of the partial ionic volumes $\bar{v}_+$ and $\bar{v}_-$ (as opposed to the partial molar volumes of water and electrolyte which can be unequivocally defined from macroscopic measurements and often found in tables of properties of electrolyte solutions). Moreover, the electrical potential difference across the membrane, $\Delta\phi$, appears in two of the three forces*, whereas the potential difference actually measured, $\Delta\phi_-$, is that between two Ag/AgCl electrodes placed at some distance from the membrane. Therefore previous investigators have performed certain transformations of the Onsager set of equations to make it directly amenable to evaluation of the experimental results. We shall critically discuss two transformations, one by Duncan (11) who initiated this project, and one found in the text of Katchalsky and Curran (2). We shall then justify the use of a modification of the latter transformation for the evaluation of our measurements and demonstrate this evaluation.**

The Duncan Transformation (11)

The purpose of this transformation is the use of driving forces which can be readily measured instead of the generalized forces in the original Onsager equations (3) - (5) which involve ionic volumes and the electrical potential difference across the membrane. The "price" paid for this simplification of the forces is the introduction of two non-conservative fluxes (i.e. fluxes which are not uniform across the membrane even in the steady state). The impact of this problem will be discussed after presenting

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*It is not easy to measure $\Delta\phi$ accurately when a current passes through the membrane.

**This transformation is referred to as the "Michaeli-Kedem" ("M-K") transformation in this report.

the transformation in elementary manner. In the following derivation consider a membrane bracketed by two solutions of the same electrolyte with a concentration difference, Δc, so small that in the steady state the difference between the volume flux, J_V, leaving one solution to enter the membrane at one face, and, after passage through the membrane, entering the other solution, is negligible*. (A similar consideration is to hold with respect to the "difference flux", J_D, to be defined later). With this reservation, it is possible to define a volume flux, J_V ($cm^3\ cm^{-2}\ sec^{-1} = cm\ sec^{-1}$) without specifying the location at which it is considered:

$$J_V = J_w\bar{v}_w + J_+\bar{v}_+ + J_-\bar{v}_- \tag{7}$$

The $\bar{v}_i$'s are the partial molar volumes of the components; one takes the average of their values in the two solutions bracketing the membrane. Substituting for the fluxes J_+, J_- and J_w from equations (3) - (5) respectively, we obtain:

$$J_V = -\Delta p\underbrace{[(L_{wv}\bar{v}_w^2 + L_{+w}\bar{v}_w\bar{v}_+ + L_{-w}\bar{v}_w\bar{v}_-) + (L_{w+}\bar{v}_w\bar{v}_+ + L_{++}\bar{v}_+^2 + L_{-+}\bar{v}_+\bar{v}_-) + (L_{w-}\bar{v}_w\bar{v}_- + L_{+-}\bar{v}_+\bar{v}_- + L_{--}\bar{v}_-^2)]}_{L_{VV}}$$

$$-\Delta\mu_w(L_{ww}\bar{v}_w + L_{+w}\bar{v}_+ + L_{-w}\bar{v}_-) - \Delta\mu_+^c(L_{w+}\bar{v}_w + L_{++}\bar{v}_+ + L_{-+}\bar{v}_-) + \Delta\mu_-^c(L_{w-}\bar{v}_w + L_{+-}\bar{v}_+ + L_{--}\bar{v}_-)$$

$$\underbrace{-\mathcal{F}\Delta\phi(L_{w+}\bar{v}_w + L_{++}\bar{v}_+ + L_{-+}\bar{v}_- - L_{w-}\bar{v}_w - L_{+-}\bar{v}_+ - L_{--}\bar{v}_-)}_{L_{VE}} \tag{8}$$

*At first sight, it might seem as if in the steady state the volume loss of one solution were numerically equal to the volume gain of the other. Inasmuch as the partial molar volumes of water and electrolyte differ somewhat with the solution concentration, volume conservation does not prevail, however, i.e. the volume loss of one solution does not quite equal the gain of the other especially if Δc is appreciable.

Now transform the center term of eq. (8) which contains the chemical potential differences, $\Delta\mu^c$, by using the Gibbs-Duhem relation [ref. 2, eq. (9-4) to substitute for $\Delta\mu_w^c$ in terms of the chemical potential of the salt, $\Delta\mu_s^c$:

$$\left(\frac{\Delta\mu_w^c}{\Delta\mu_s^c}\right)_T = -\frac{\bar{c}_s}{\bar{c}_w} \tag{9}$$

(valid for small concentration differences between the two solutions). $\bar{c}_s$ and $\bar{c}_w$ are the averages of the salt and water concentrations in the two solutions respectively. Also substitute for the potential difference across the membrane, $\Delta\phi$, in terms of the measured potential difference between the Ag/AgCl electrodes, $\Delta\phi_-$, from eq. (A1-17):

$$-\mathcal{F}\Delta\phi = -\mathcal{F}\Delta\phi_- - \Delta\mu_-^c \tag{10}$$

This transformation yields

$$J_V = L_{VV}(-\Delta p) + \Delta\mu_s^c\left(L_{ww}\bar{v}_w\frac{\bar{c}_s}{\bar{c}_w} + L_{+w}\bar{v}_+\frac{\bar{c}_s}{\bar{c}_w} + L_{-w}\bar{v}_-\frac{\bar{c}_s}{\bar{c}_w}\right) - \Delta\mu_+^c\left(L_{w+}\bar{v}_w + L_{++}\bar{v}_+ + L_{-+}\bar{v}_-\right)$$

$$- \Delta\mu_-^c\left(L_{w-}\bar{v}_w + L_{+-}\bar{v}_+ + L_{--}\bar{v}_-\right) + L_{VE}(-\mathcal{F}\Delta\phi_-) - \Delta\mu_-^c\left(L_{w+}\bar{v}_w + L_{++}\bar{v}_+ + L_{-+}\bar{v}_- - L_{w-}\bar{v}_w - L_{+-}\bar{v}_+ - L_{--}\bar{v}_-\right) \tag{11}$$

The chemical potential of the salt, μ_s^c, is the sum of the chemical potentials of its constituent ions. Therefore

$$\Delta\mu_s^c = \Delta\mu_+^c + \Delta\mu_-^c \tag{12}$$

Hence eq. (11) reduces to

$$J_V = L_{VV}(-\Delta p) + \underbrace{[L_{w+}\bar{v}_w + L_{++}\bar{v}_+ + L_{-+}\bar{v}_- - \frac{\bar{c}_s}{\bar{c}_w}(L_{ww}\bar{v}_w + L_{+w}\bar{v}_+ + L_{-w}\bar{v}_-)]}_{L_{VD}} (-\Delta\mu_s^c) + L_{VE}(-\mathcal{F}\Delta\phi_-) \quad (13)$$

The second flux used in the Duncan transformation is the "separation flow", J_D (mole cm^{-2} sec^{-1}) which is proportional to the velocity, u_s, of the salt relative to that of the water, u_w (ref. 2, p. 99).

$$\lim_{\Delta c \to 0} J_D \equiv J_s - \frac{c_s}{c_w} J_w = c_s(u_s - u_w) \quad (14)$$

In the steady state, the fluxes J_s and J_w are uniform, but since the concentrations vary across the membrane, J_D, u_s and u_w are not uniform ("conservative"). Again, for small concentration differences this non-uniformity is neglected and average values of the parameters are used:

$$J_D = J_s - \frac{\bar{c}_s}{\bar{c}_w} J_w \quad (15)$$

In the experimental system considered here the salt flux, J_s, is equal in magnitude to the flux of sodium ions, J_+ (both being measured in mole cm^{-2} sec^{-1}), because to maintain electroneutrality, the Ag/AgCl electrodes supply and subtract an equivalent amount of Cl^- for the amount of Na^+ entering or leaving a compartment respectively:

$$J_s = J_+ \quad (16)$$

Substituting J_+ for J_s in eq. (15), and then substituting the expressions for J_+ and J_w from the original flux equations (3) and (4) respectively, we

obtain

$$J_D = J_+ - \frac{\bar{c}_s}{\bar{c}_w} J_w = \underbrace{-\Delta p\left[(L_{+w}\bar{v}_w + L_{++}\bar{v}_+ + L_{+-}\bar{v}_-) - L_{ww}\bar{v}_w \frac{\bar{c}_s}{\bar{c}_w} - L_{w+}\bar{v}_+ \frac{\bar{c}_s}{\bar{c}_w} - L_{w-}\bar{v}_- \frac{\bar{c}_s}{\bar{c}_w}\right]}_{L_{DV}}$$

$$-\Delta\mu_w^c\left(L_{+w} - \frac{\bar{c}_s}{\bar{c}_w} L_{ww}\right) - \Delta\mu_+^c\left(L_{++} - \frac{\bar{c}_s}{\bar{c}_w} L_{w+}\right) - \Delta\mu_-^c\left(L_{+-} - \frac{\bar{c}_s}{\bar{c}_w} L_{w-}\right)$$

$$\underbrace{-\mathcal{F}\Delta\phi_-\left(L_{++} - \frac{\bar{c}_s}{\bar{c}_w} L_{w+} - L_{+-} + \frac{\bar{c}_s}{\bar{c}_w} L_{w-}\right)}_{L_{DE}} - \Delta\mu_-^c\left(L_{++} - \frac{\bar{c}_s}{\bar{c}_w} L_{w+} - L_{+-} + \frac{\bar{c}_s}{\bar{c}_w} L_{w-}\right) \qquad (17)$$

Combining the terms containing $\Delta\mu_+^c$ with those containing $\Delta\mu_-^c$ by use of eq. (12) we obtain

$$J_D = L_{DV}(-\Delta p) + (-\Delta\mu_s^c)\left(L_{++} - \frac{\bar{c}_s}{\bar{c}_w} L_{w+}\right) + \left(-\Delta\mu_w^c\right)\left(L_{+w} - \frac{\bar{c}_s}{\bar{c}_w} L_{ww}\right) + L_{DE}(-\mathcal{F}\Delta\phi_-) \qquad (18)$$

Substituting for $\Delta\mu_w^c$ in terms of the chemical potential of the salt, $\Delta\mu_s^c$, by use of the Gibbs-Duhem equation (9), we obtain

$$J_D = L_{DV}(-\Delta p) + (-\Delta\mu_s^c)\underbrace{\left(L_{++} - \frac{\bar{c}_s}{\bar{c}_w} L_{w+} - L_{+w}\frac{\bar{c}_s}{\bar{c}_w} + \frac{\bar{c}_s^2}{\bar{c}_w^2} L_{ww}\right)}_{L_{DD}} + L_{DE}(-\mathcal{F}\Delta\phi_-) \qquad (19)$$

Finally, the current density, i (amp cm^{-2}) divided by Faraday's constant (coul eq^{-1}) is the third flux in Duncan's set of flux equations. In the steady state, this flux is conservative, because of electroneutrality. By using the expressions for J_+ and J_- from the original flux equations (3) and

(4) we obtain

$$i/\mathcal{F} = J_+ - J_- = (-\Delta p)\underbrace{(L_{+w}\bar{v}_w - L_{-w}\bar{v}_w) + (L_{++}\bar{v}_+ - L_{-+}\bar{v}_+) + (L_{+-}\bar{v}_- - L_{--}\bar{v}_-)]}_{L_{EV}}$$

$$-\Delta\mu_w^c(L_{+w} - L_{-w}) - \Delta\mu_+^c(L_{++} - L_{-+}) - \Delta\mu_-^c(L_{+-} - L_{--})$$

$$\underbrace{-\mathcal{F}\Delta\phi(L_{++} - L_{-+} - L_{+-} + L_{--})}_{L_{EE}} \qquad (20)$$

Substituting for $-\Delta\mu_w^c$ from the Gibbs-Duhem equation (9) and for $-\mathcal{F}\Delta\phi$ from (10) we obtain

$$i/\mathcal{F} = L_{EV}(-\Delta p) - \Delta\mu_s^c\left(-L_{+w}\frac{\bar{c}_s}{\bar{c}_w} + L_{-w}\frac{\bar{c}_s}{\bar{c}_w}\right) - \Delta\mu_+^c(L_{++} - L_{-+}) - \Delta\mu_-^c(L_{+-} - L_{--})$$

$$+ L_{EE}(-\mathcal{F}\Delta\phi_-) - \Delta\mu_-^c(L_{++} - L_{-+} - L_{+-} + L_{--}) \qquad (21)$$

Combining the terms containing $\Delta\mu_+^c$ and $\Delta\mu_-^c$ by means of eq. (12), we obtain

$$i/\mathcal{F} = L_{EV}(-\Delta p) + \underbrace{\left(L_{++} - L_{-+} + L_{-w}\frac{\bar{c}_s}{\bar{c}_w} - L_{+w}\frac{\bar{c}_s}{\bar{c}_w}\right)}_{L_{ED}}(-\Delta\mu_s^c) + L_{EE}(-\mathcal{F}\Delta\phi_-) \qquad (22)$$

It is seen that if the reciprocity relations [eq. (6)] are satisfied in the original flux equations (3) - (5), i.e. if $L_{+-} = L_{-+}$, $L_{+w} = L_{w+}$, $L_{-w} = L_{w-}$, then there is also reciprocity in the transformed equations, i.e. $L_{VD} = L_{DV}$, $L_{VE} = L_{EV}$, $L_{DE} = L_{ED}$. We conclude therefore that in the transformed equations, the fluxes J_V, J_D and $(i/\mathcal{F})$ are properly conjugated to the driving

forces $-\Delta p$, $-\Delta\mu_s^c$ and $-\mathcal{F}\Delta\phi_-$ respectively. In summary the three transformed flux equations (13), (17) and (22) are rewritten here:

$$J_V = L_{VV}(-\Delta p) + L_{VD}(-\Delta\mu_s^c) + L_{VE}(-\mathcal{F}\Delta\phi_-) \quad (23)$$

$$J_D = L_{DV}(-\Delta p) + L_{DD}(-\Delta\mu_s^c) + L_{DE}(-\mathcal{F}\Delta\phi_-) \quad (24)$$

$$i/\mathcal{F} = L_{EV}(-\Delta p) + L_{ED}(-\Delta\mu_s^c) + L_{EE}(-\mathcal{F}\Delta\phi_-) \quad (25)$$

"Duncan set of flux equations"

It should be noted that the equations given by Duncan in ref. (11b) are arranged in somewhat different form; specifically in the last equation $-\mathcal{F}\Delta\phi_-$ appears on the left and $i/\mathcal{F}$ on the right; also the terms containing the driving force $-\mathcal{F}\Delta\phi$ in equations (23) and (24) have been replaced by terms containing the conjugated flux, $i/\mathcal{F}$, instead. Since both the driving forces and the fluxes in eqs. (23) - (25) are almost identical with those in ref. (11b), however, we feel justified in applying the term "Duncan set of flux equations" to eqs. (23) - (25).

Table 1 lists the conductance coefficients, L, in the Duncan set of flux equations in terms of the original coefficients in the Onsager set, eqs. (3) - (5).

The relative simplicity of equations (23) - (25) derives in part from the fact that they contain the measurable potential difference, $\Delta\phi_-$, between the Ag/AgCl electrodes rather than the potential difference, $\Delta\phi$, across the membranes which can only be calculated if assumptions are made about the difference of individual electrode potentials or junction potentials (14).

TABLE 1

Relations Between Conductance Coefficients in Onsager-Type Set of Flux Equations (3) - (5)* and Transformed Set (B. C. Duncan), Eqs. (23) - (25)

$L_{VV} = L_{++}\bar{v}_+^2 + L_{--}\bar{v}_-^2 + \bar{v}_+\bar{v}_w(L_{w+} + L_{+w}) + \bar{v}_-\bar{v}_w(L_{w-} + L_{-w}) + \bar{v}_+\bar{v}_-(L_{+-} + L_{-+}) + L_{ww}\bar{v}_w^2$	cm sec^{-1} $dekabar^{-1}$
$L_{DD} = L_{++} + (\bar{c}_s/\bar{c}_w)^2 L_{ww} - (\bar{c}_s/\bar{c}_w)(L_{+w} + L_{w+})$	$mole^2$ $joule^{-1}$ cm^{-2} sec^{-1}
$L_{EE} = L_{++} + L_{--} - (L_{+-} + L_{-+})$	$mole^2$ $joule^{-1}$ cm^{-2} sec^{-1}
$L_{VD} = (L_{++}\bar{v}_+ + L_{-+}\bar{v}_- + L_{w+}\bar{v}_w) - (\bar{c}_s/\bar{c}_w)(L_{+w}\bar{v}_+ - L_{-w}\bar{v}_- + L_{ww}\bar{v}_w)$	mole $joule^{-1}$ cm sec^{-1}
$L_{DV} = (L_{++}\bar{v}_+ + L_{+-}\bar{v}_- + L_{+w}\bar{v}_w) - (\bar{c}_s/\bar{c}_w)(L_{w+}\bar{v}_+ - L_{w-}\bar{v}_- + L_{ww}\bar{v}_w)$	mole $joule^{-1}$ cm sec^{-1}
$L_{VE} = \bar{v}_+(L_{++} - L_{+-}) + \bar{v}_-(L_{-+} - L_{--}) + \bar{v}_w(L_{w+} - L_{w-})$	mole $joule^{-1}$ cm sec^{-1}
$L_{EV} = \bar{v}_+(L_{++} - L_{-+}) + \bar{v}_-(L_{+-} - L_{--}) + \bar{v}_w(L_{+w} - L_{-w})$	mole $joule^{-1}$ cm sec^{-1}
$L_{DE} = (L_{++} - L_{+-}) - (\bar{c}_s/\bar{c}_w)(L_{w+} - L_{w-})$	$mole^2$ $joule^{-1}$ cm^{-2} sec^{-1}
$L_{ED} = (L_{++} - L_{-+}) - (\bar{c}_s/\bar{c}_w)(L_{+w} - L_{-w})$	$mole^2$ $joule^{-1}$ cm^{-2} sec^{-1}

*All Onsager coefficients, L_{ij}, have the units $mole^2$ $joule^{-1}$ cm^{-2} sec^{-1}.

On the other hand, the use of the non-uniform fluxes J_V and J_D limits the direct utilization of these equations to systems with very small concentration differences between the two solutions bracketing the membrane.

The Michaeli-Kedem Transformation (2, p. 151, 15)

This transformation leads to three fluxes, J_s, J_w and $i/\mathcal{F}$, which are all uniform in the steady state. Moreover the three conjugated forces, $\{-\Delta\mu_s\}$, $\{-\Delta\mu_w\}$ and $\Delta\tilde{\mu}_- = -\mathcal{F}\Delta\phi_- + (\bar{v}_{AgCl} - \bar{v}_{Ag})\,\Delta p$ can be readily measured and/or found in thermodynamic tables. For this reason we have now come to the conclusion that this set of equations is the most practical for the evaluation of our past and present transport experiments, and that the L-conductance coefficients in this matrix are the most practical for characterizing the transport properties of the membrane. [It should be noted that we consider this type of characterization as an important intermediate step, but plan to eventually use friction coefficients (8 - 10) for membrane characterization].

The starting point for this transformation is the original (Onsager) set of flux equations (3) - (5) which is rewritten, using the symbol $\Delta\tilde{\mu}_i$ for the difference between the total potentials of component i in the right and left solution respectively [see also eq. (A1-1) in the appendix]:

$$\Delta\tilde{\mu}_i \equiv \Delta\mu_i + z_i\mathcal{F}\Delta\phi = \bar{v}_i\Delta p + \Delta\mu_i^c + z_i\mathcal{F}\Delta\phi \qquad (26)$$

Since the net charge of water, z_w, is zero $\Delta\tilde{\mu}_w = \Delta\mu_w$.

With this notation, the set of original Onsager flux equations is

$$J_+ = L_{++}(-\Delta\tilde{\mu}_+) + L_{+-}(-\Delta\tilde{\mu}_-) + L_{+w}(-\Delta\mu_w) \tag{27}$$

$$J_- = L_{-+}(-\Delta\tilde{\mu}_+) + L_{--}(-\Delta\tilde{\mu}_-) + L_{-w}(-\Delta\mu_w) \tag{28}$$

$$J_w = L_{w+}(-\Delta\tilde{\mu}_+) + L_{w-}(-\Delta\tilde{\mu}_-) + L_{ww}(-\Delta\mu_w) \tag{29}$$

The total potential of the salt component, $\Delta\tilde{\mu}_s$, is equal to the sum of the total potentials of the constituent ions. Also, since salt carries no net charge, $z_s = 0$, and hence $\Delta\tilde{\mu}_s = \Delta\mu_s$:

$$\Delta\tilde{\mu}_s = \Delta\tilde{\mu}_+ + \Delta\tilde{\mu}_- \tag{30}$$

We substitute $\Delta\mu_s - \Delta\tilde{\mu}_-$ for $\Delta\tilde{\mu}_+$ in eqs. (27)-(29) and then $-\mathcal{F}\Delta\phi_- + v_{Cl}\Delta p$ for $\Delta\tilde{\mu}_-$ from eq. (A1-14) in the appendix. The result is the following set of equations:

$$J_+ = J_s = L_{++}(-\Delta\mu_s) + (L_{++} - L_{+-})\,(-\mathcal{F}\Delta\phi_- + v_{Cl}\Delta p) + L_{+w}(-\Delta\mu_w) \tag{31}$$

$$J_- = L_{-+}(-\Delta\mu_s) + (L_{-+} - L_{--})\,(-\mathcal{F}\Delta\phi_- + v_{Cl}\Delta p) + L_{-w}(-\Delta\mu_w) \tag{32}$$

$$J_w = L_{w+}(-\Delta\mu_s) + (L_{w+} - L_{w-})\,(-\mathcal{F}\Delta\phi_- + v_{Cl}\Delta p) + L_{ww}(-\Delta\mu_w) \tag{33}$$

Finally, we calculate $i/\mathcal{F}$ from eqs. (31) and (32):

$$i/\mathcal{F} = J_+ - J_- = (L_{++} - L_{-+})(-\Delta\tilde{\mu}_s) + (L_{++} - L_{+-} - L_{-+} + L_{--})(-\mathcal{F}\Delta\phi_- + v_{Cl}\Delta p) + (L_{+w} - L_{-w})(-\Delta\mu_w) \tag{34}$$

Summarizing, the transformed set of flux equations (31), (33) and (34) is:

$$J_s = L_{ss}(-\Delta\mu_s) + L_{sw}(-\Delta\mu_w) + L_{se}(-\mathcal{F}\Delta\phi_- + v_{Cl}\Delta p) \quad (35)$$

$$J_w = L_{ws}(-\Delta\mu_s) + L_{ww}(-\Delta\mu_w) + L_{we}(-\mathcal{F}\Delta\phi_- + v_{Cl}\Delta p) \quad (36)$$

$$i/\mathcal{F} = L_{es}(-\Delta\mu_s) + L_{ew}(-\Delta\mu_w) + L_{ee}(-\mathcal{F}\Delta\phi_- + v_{Cl}\Delta p) \quad (37)$$

"Modified M-K set of flux equations"

where the meaning of the new L conductance coefficients in terms of those of the original set, eqs. (3)-(5) is shown in Table 2. Note that when reciprocity [eq. (6)] is satisfied in the original set, reciprocity also prevails in the transformed one. We conclude that in eqs. (35)-(37) fluxes and forces are properly conjugated.

Experimental Results

Since the "concentration-clamp" apparatus and the operating procedure have been described in detail in previous reports and in a recent publication from this project (16), no details about these aspects of the work are presented here. The cell for the measurement of the membrane conductivity and the measurement procedure have been described in Quarterly Report No. 12, Section A. III. 4 (p. 15-17) and therefore they are not repeated here either. The results used for the calculation of the L-coefficients are listed in Table 3. In addition, we shall use the value of 5.7 ± 0.8 ohm cm^2 for the resistance of one cm^2 of active (uncovered) membrane area. This value

TABLE 2

Relations Between Conductance Coefficients in Onsager-Type Flux Equations (3)-(5) and Transformed Set (I. Michaeli and O. Kedem) Eqs. (35)-(37)

$$L_{ss} = L_{++}$$

$$L_{ww} = L_{ww}$$

$$L_{ee} = L_{++} - L_{+-} - L_{-+} + L_{--}$$

$$L_{sw} = L_{+w}$$

$$L_{ws} = L_{w+}$$

$$L_{se} = L_{++} - L_{+-}$$

$$L_{es} = L_{++} - L_{-+}$$

$$L_{we} = L_{w+} - L_{w-}$$

$$L_{ew} = L_{+w} - L_{-w}$$

All coefficients have the units $mole^2\ joule^{-1}\ cm^{-2}\ sec^{-1}$.

TABLE 3

Experimental Results Used to Calculate M-K Conductance Coefficients, L

Experiment No.	163	159	150	145
Type	Permeation under pressure		Electromigration - electroosmosis	Dialysis↔ osmosis
Pressure difference, Δp, atm	-1	-0.8	0	0
Salt concentration on right*, c''_s, mole cm^{-3}	10^{-4}	10^{-4}	10^{-4}	$1.001_6 \times 10^{-4}$
Salt concentration on left*, c'_s, mole cm^{-3}	10^{-4}	10^{-4}	10^{-4}	$0.495_4 \times 10^{-4}$
Concentration difference, Δc_s, mole cm^{-3}	0	0	0	$0.506_2 \times 10^{-4}$
Current density, i, ma cm^{-2}**	0	0	-0.971	0
J_V*** cm $sec^{-1} \times 10^6$	0.374	0.304	-1.805	0.284
Salt flux, J_s, mole cm^{-2} $sec^{-1} \times 10^9$			-8.69	-0.0713
Water flux, J_w, mole cm^{-2} $sec^{-1} \times 10^9$			-99.79	15.3
Potential difference, $\Delta\phi_-$, volt $\times 10^6$				
Cation transport number, t_+			0.864	
Water transport number, t_w			9.63	
Streaming potential, $\Delta\phi_-$, volt $\times 10^3$	0.174	0.146		

*Buret side, right; column side, left; see Figure 1. c determined by chloride titration.

**Positive electrode on right side. Active membrane area 8.13 cm^2.

***Calculated from data on the right (buret) side only.

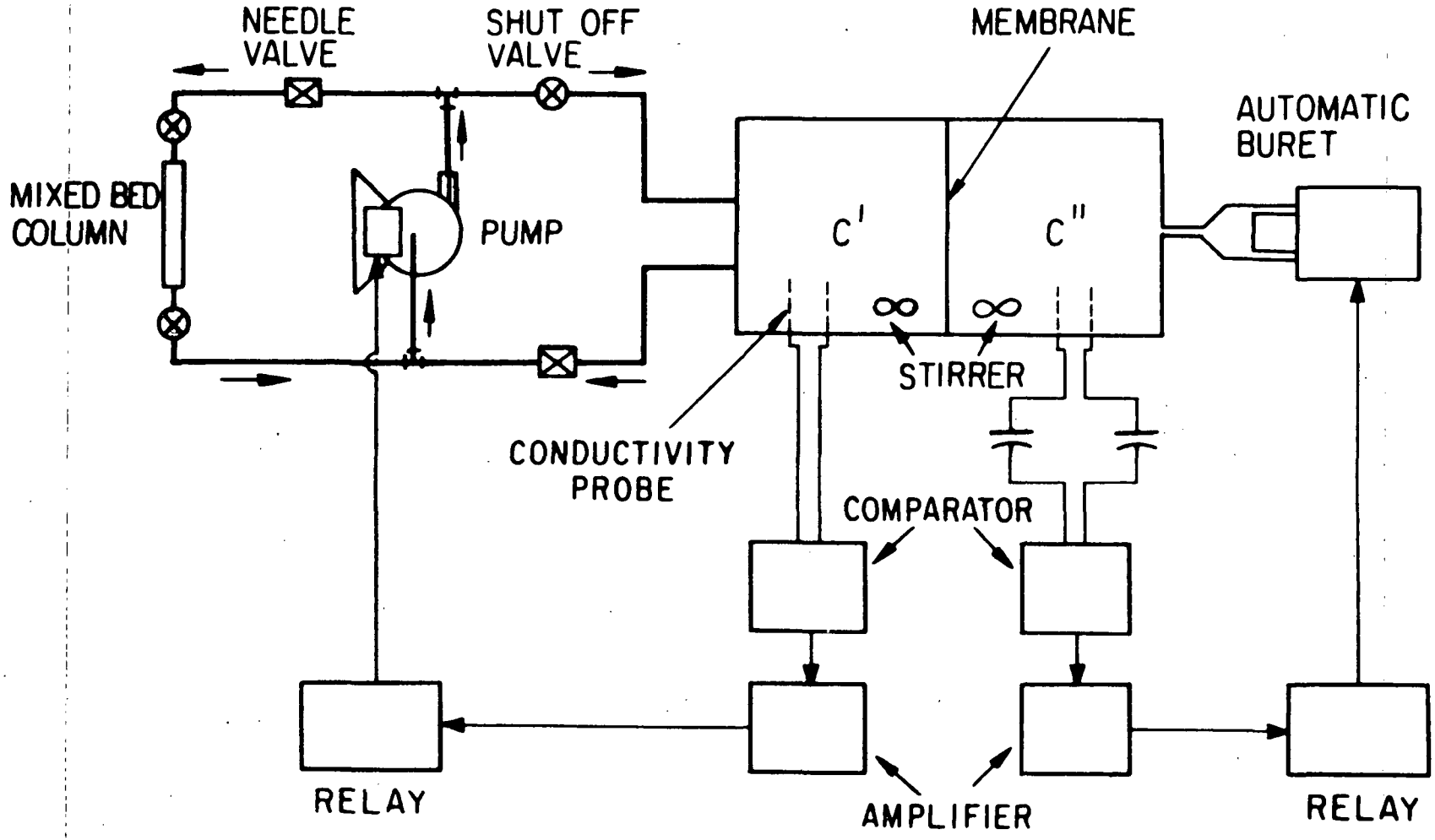

FIGURE 1. SCHEMATIC REPRESENTATION OF THE CONCENTRATION FEEDBACK MECHANISM

corresponds to recent results obtained in the conductance cell described in Progress Report No. 12. [The active area of the membrane (not covered by perforated supports) was 20.2 cm^2 and the membrane thickness 0.017 cm]. A recent critical reexamination of the raw data from the measurements, described in Progress Report No. 13, and observation of a progressive change in the color of the active areas of the membrane made it seem advisable to remeasure the resistance. In the process of remeasurement, the procedure was refined and additional measurements by this new procedure are in progress. (It should be noted that exact measurements of the resistance of thin, conductive membranes are by no means a simple matter.) Results of the newest measurements evaluated, which will hopefully be more accurate, should be available soon.

Method for Calculation of the L-Conductance Coefficients for the M-K Transport Equations

In the strict sense the Michaeli-Kedem ("M-K") transport equations, (35)-(37) apply to the total system between the electrodes, i.e. the membrane plus the two adjacent solutions. Since we are primarily interested in the transport coefficients of the membrane proper, we inquire first which of the fluxes and forces would be appreciably affected if we progressively reduced the thickness of the solution layers in series with the membrane.

Since the solutions are well-stirred, concentration gradients in them are negligible. Thus the generalized forces $-\Delta\mu_s$ and $-\Delta\mu_w$ which represent the chemical potential differences between the solutions near the electrodes

are identical with the corresponding differences across the membranes only. As for the electrical potential difference, $\Delta\phi_-$, it will depend on the magnitude of the current density, i. When the latter is zero, $\Delta\phi_-$ will be independent of the position of the electrodes, and hence the experimental $\Delta\phi_-$ measured at a finite distance, can be substituted for the corresponding potential difference of electrodes in very close vicinity of the membranes. When the current density is finite, however, and kept constant, moving the electrodes towards the membrane will decrease the absolute value of $\Delta\phi_-$, since the $i\rho$ drop through the solutions is decreased. Therefore, if we want to calculate transport coefficients for the membrane only, without contribution of the solution layers, we have to make allowance for this $i\rho$ drop, i.e. instead of using the measured values of $\Delta\phi_-$, we use the value corrected for infinitesimally small distance from the membrane:

$$(\Delta\phi_-)_{\text{across membrane}} = (\Delta\phi_-)_{\text{measured}} + i(\rho' z' + \rho'' z'') \qquad (38)$$

where the ρ's are the specific resistances of the solutions and the z's the distances between the membrane surfaces and the electrode surfaces in the two solutions respectively.

This is exactly what our method of measuring the membrane conductance in the cell with the movable electrodes makes possible.* Moreover, when the current is negligible (e.g. in measurements of streaming potentials or membrane potentials), it is seen from eq. (38) that the measured potential differences are independent of the position of the electrodes.

*The cell is described in Quarterly Report No. 12.

In a thought experiment one can reduce all the L-coefficients to a system in which the electrodes are so close to the membrane surface that the mass and ion-transfer resistances of the remaining thin solution layers are entirely negligible. The L-coefficients calculated for this system may be considered as the transport coefficients for the membrane.

The methods of calculation of the conductance coefficients from the experiments described in Table 3 are presented in this section. The numerical calculations are in Section A. 2. of the Appendix.

$\underline{L_{ee}}$

When the solutions are of the same concentration and at the same pressure, the algebraic sum of the two Ag/AgCl electrode potentials (i.e. of the potential drops between each silver metal and the solution in contact with it) is zero. Therefore in this case $\Delta\phi_- = \Delta\phi$. Since the conductivity of the membrane is defined as

$$\kappa \equiv (-i/\Delta\phi)d \qquad (39)^*$$

if follows from eq. (37) that

$$(L_{ee})_{\Delta\mu=0} = -i/(\Delta\phi_-\mathcal{F}^2) = -i/(\Delta\phi\mathcal{F}^2) = \kappa/(\mathcal{F}^2 d) = (\mathcal{F}^2\rho d)^{-1} \qquad (40)$$

In the determination of the membrane resistance (per unit active area), ρd, the solution resistance is eliminated by extrapolation to zero solution thickness. Hence $(L_{ee})_{\Delta\mu=0}$ is a transport characterization

*The negative sign derives from the convention that for positive potential difference ($\phi'' > \phi'$), the current direction (always taken as the flow direction of positive carriers) is negative.

constant of the membrane alone. In this measurement, platinized platinum electrodes carrying alternating current were used, but for $\Delta\mu=0$ this makes no difference, since in this case, the electric potential difference between these electrodes is the same as $\Delta\phi_{-}$.

$\underline{L_{se}}$

Dividing eq. (35) by (37) for $\Delta\mu=0$, we obtain

$$L_{se}/L_{ee} = [J_s/(i/\mathcal{F})]_{\Delta\mu=0} \equiv t_+ \tag{41}$$

Hence

$$(L_{se})_{\Delta\mu=0} = t_+(L_{ee})_{\Delta\mu=0} \tag{42}$$

$(J_s)_{\Delta\mu=0}$ is experimentally determined in an electromigration - electroosmosis experiment (e.g. No. 150, Table 1). The calculation of $(L_{ee})_{\Delta\mu=0}$ from a membrane resistance measurement has already been described [eq. (40)]. Hence L_{se} can be calculated from eq. (42).

$\underline{L_{we}}$

Dividing eq. (36) by (37) for $\Delta\mu=0$, we obtain

$$L_{we}/L_{ee} = [J_w/(i/\mathcal{F})]_{\Delta\mu=0} \equiv t_w \tag{43}$$

Hence

$$(L_{we})_{\Delta\mu=0} = t_w(L_{ee})_{\Delta\mu=0} \tag{44}$$

Thus $(L_{we})_{\Delta\mu=0}$ can be determined from an electromigration - electroosmosis experiment, simultaneously with and similar to the determination of L_{se}.

L_{es} and L_{ew}

In eq. (37) we substitute for $\Delta\mu_w$ from the Gibbs-Duhem equation (9), and setting

$$\Delta\mu_w = \Delta\mu_w^c + \bar{v}_w \Delta p \tag{45}$$

[from eq. (26), with $z_w = 0$], we obtain the following equation for the electric current density*

$$i = \mathcal{F}[(L_{es}\bar{v}_s + L_{ew}\bar{v}_w)(-\Delta p) + (L_{es} - L_{ew}\frac{\bar{c}_s}{\bar{c}_w})(-\Delta\mu_s^c) - L_{ee}(\mathcal{F}\Delta\phi_- + \Delta p v_{Cl})] \tag{46}$$

This equation can be used to evaluate measurements of the streaming potential, which are usually performed with an electrometer or other device which draws extremely little electric current. Setting $i = 0$ we obtain from eq. (46)

$$-\Delta\phi_- = \frac{L_{es} - L_{ew}(\bar{c}_s/\bar{c}_w)}{\mathcal{F} L_{ee}} \Delta\mu_s^c + \frac{1}{\mathcal{F}}\left(\frac{L_{es}\bar{v}_s + L_{ew}\bar{v}_w}{L_{ee}} - v_{Cl}\right)\Delta p \tag{47}$$

Thus a plot of the potential difference between the two Ag/AgCl electrodes in the two half-cells, $-\Delta\phi_- \equiv \phi_-' - \phi_-''$ versus the pressure difference, Δp, should be a straight line. In general, the two unknowns, L_{ew} and L_{es}, can be determined by solution of the simultaneous equations for the slope ("streaming potential differential, SPD") and the ordinate intercept ("membrane potential, MP"):

---

*Since the Gibbs-Duhem relation is not exactly satisfied for finite concentration differences (see footnote p. 49), we plan to use $\Delta\mu_s$ and $\Delta\mu_w$ separately in the future without relying on this relation for the calculation of L_{es} and L_{ew}.

$$\frac{\partial(-\Delta\phi_-)}{\partial(\Delta p)} \equiv \text{SPD} = \frac{1}{\mathcal{F}}\left(\frac{L_{es}\bar{v}_s + L_{ew}\bar{v}_w}{L_{ee}} - v_{Cl}\right) \tag{48}$$

$$(\Delta\phi_-)_{\Delta p=0} \equiv \text{MP} = \frac{L_{es} - L_{ew}(\bar{c}_s/\bar{c}_w)}{\mathcal{F} L_{ee}} \Delta\mu_s^c \tag{49}$$

At the present stage of this research, we have reliable streaming potential lines only for a system without concentration gradient (i.e. $\Delta\mu_s^c = 0$). Such lines are shown in Figs. 2 and 3. Inasmuch as the membrane potential is zero these data can yield only $L_{es}\bar{v}_s + L_{ew}\bar{v}_w$, rather than L_{es} and L_{ew} separately. Therefore, for the purpose of this interim report, we have <u>assumed</u> (rather than proven) that the following reciprocity is satisfied, as the theory demands*:

$$L_{es} = L_{se} \tag{50}$$

Since L_{se} could be calculated from the measured transport number of the cation [eq. (42)], L_{ew} could then be calculated by rearranging eq. (48)

$$(L_{ew})_{\Delta\mu=0} = \frac{1}{\bar{v}_w}\left[L_{ee}\left(\mathcal{F}\frac{\partial(-\Delta\phi_-)}{\partial(\Delta p)} + v_{Cl}\right) - L_{se}\bar{v}_s\right] \tag{51}$$

---

*This amounts essentially to assuming that the cation transport number determined by an electromigration - electroosmosis experiment agrees with that calculated from a suitable measurement of the membrane potential (17). This assumption has been made long ago for many membranes [see, for instance, (18)], although the relatively small contribution of the water transport to the membrane potential has not always been duly taken into account.

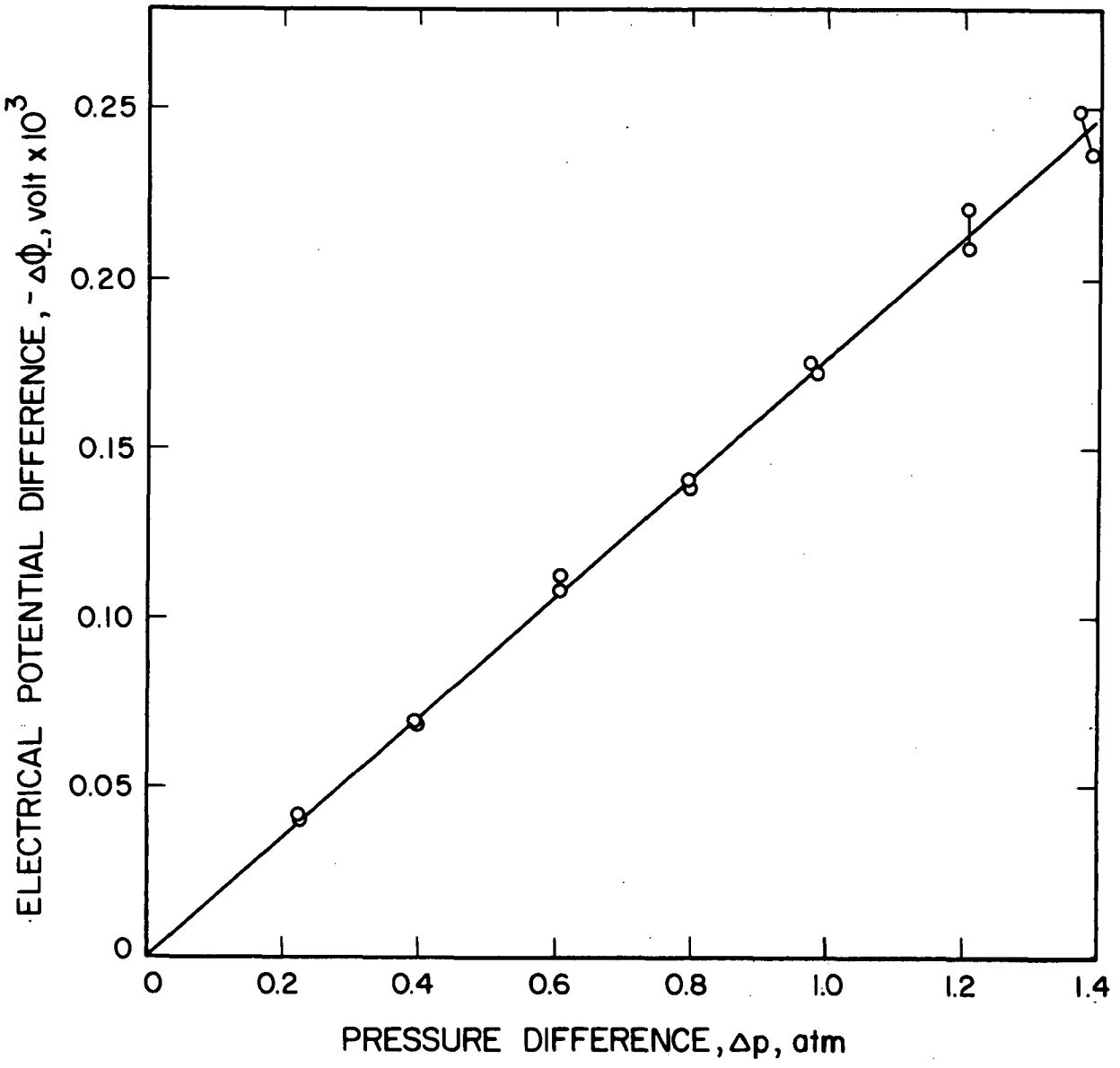

FIGURE 2. Streaming Potential Across C-103 Membrane (Experiment 157)

Solutions 0.1 M NaCl. Short vertical and slanted lines connecting points referring to same pressure setting indicate hysteresis effect after removal and re-application of pressure. All points corrected for small asymetry potentials between Ag/AgCl electrodes separated by the membrane, observed at the time of pressure release.

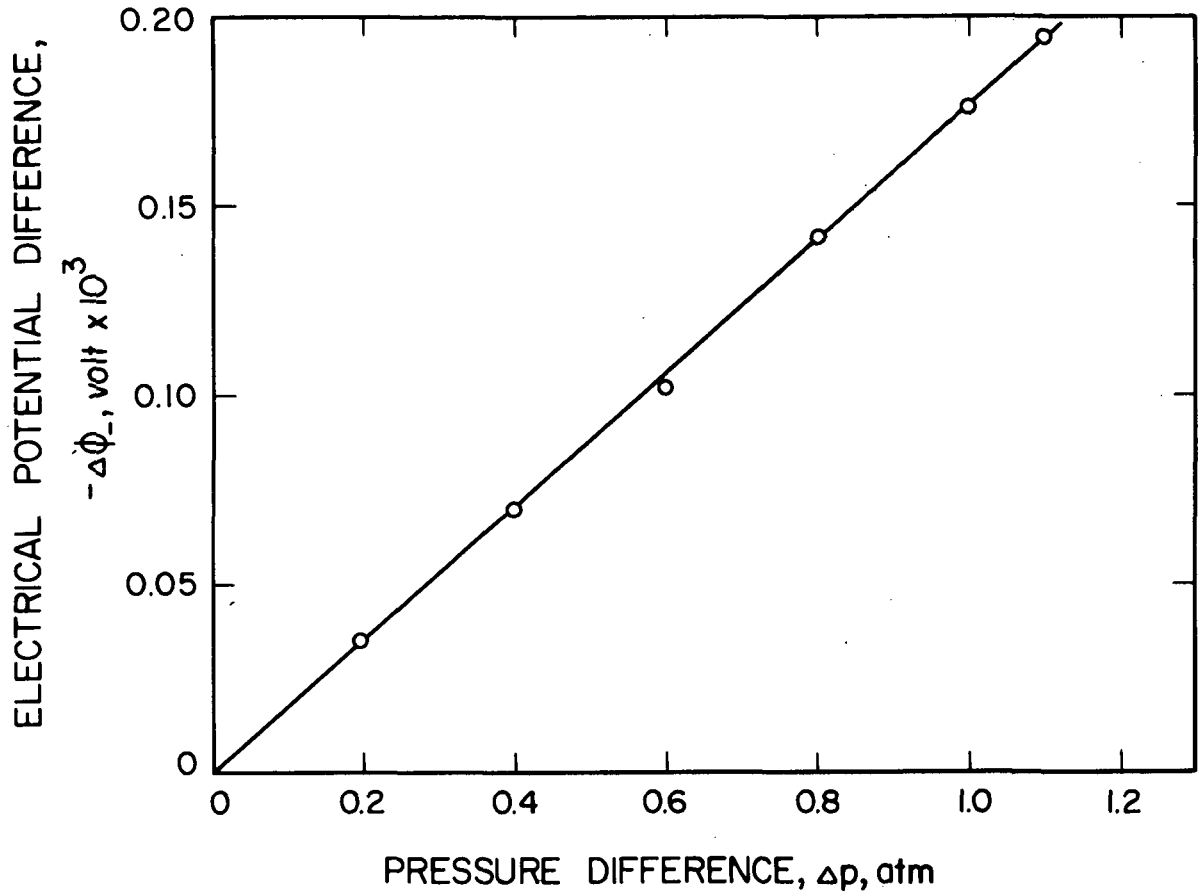

FIGURE 3. Streaming Potential Across C-103 Membrane (Experiment 162)

Solutions 0.1 M NaCl. Pressure was increased in steps without intermediate pressure release after each step. Line is corrected for small initial asymetry potential between Ag/AgCl electrodes separated by the membrane.

$$(L_{ew})_{\Delta\mu=0} = (1/\bar{v}_w)[\mathcal{F} L_{ee}(SPD + \frac{v_{Cl}}{\mathcal{F}}) - L_{se}\bar{v}_s] \quad (52)$$

In this manner we tested the reciprocity relation

$$(L_{ew})_{\Delta\mu=0} = (L_{we})_{\Delta\mu=0} \quad (53)$$

and found it to hold within six percent over the limited pressure range investigated (up to $\Delta p = -1$ atm). The numerical calculations are presented in Appendix 2.

In the future we plan to measure streaming potential curves (including measurements at $\Delta p=0$, i.e. membrane potential measurements) for systems with a concentration gradient. The assumption $L_{se} = L_{es}$ can then be tested experimentally.

L_{ss}, L_{ww}, L_{sw} and L_{ws}

These remaining four coefficients can in principle be calculated from the following four ratios of flux to driving force:

$(J_w/\Delta\mu_s^c)_{i=0,\Delta p=0}$	Osmotic water flux	(osmosis ↔ dialysis experiment)
$(J_s/\Delta\mu_s^c)_{i=0,\Delta p=0}$	Dialytic salt flux	(osmosis ↔ dialysis experiment)
$(J_w/\Delta p)_{i=0}$	Water flux	(hyperfiltration experiment)
$(J_s/\Delta p)_{i=0}$	Salt flux	(hyperfiltration experiment)

The first three of these measurements can be performed in the present "concentration-clamp" apparatus, but the accurate determination of the salt flux due to a pressure difference is not possible in this apparatus

which for a number of good reasons was built from a translucent polycarbonate plastic. The latter is not mechanically stable at pressures high enough to measure the salt-filtering effect in hyperfiltration ("reverse osmosis") with a reasonable degree of accuracy*. Therefore we assume, rather than prove, that $L_{sw} = L_{ws}$; as a result we have only three unknowns to be determined from the first three measurements. The relevant equations are derived in the following.

For i=0, we rearrange eq. (37) as follows:

$$-(\mathcal{F}\Delta\phi_{-} - v_{Cl}\Delta p) = \frac{L_{es}}{L_{ee}}\Delta\mu_s + \frac{L_{ew}}{L_{ee}}\Delta\mu_w \tag{54}$$

Applying this equation to the calculation of the salt flux in a dialysis $\leftrightarrow$ osmosis experiment (where i=0) from eq. (35) in which we substitute $-(\bar{v}_i\Delta p + \Delta\mu_i^c) = -\Delta\mu_i$ for the first two driving forces, we obtain

$$(J_s)_{i=0} = L_{ss}(-\bar{v}_s\Delta p - \Delta\mu_s^c) + L_{sw}(-\bar{v}_w\Delta p - \Delta\mu_w^c) + \frac{L_{se}}{L_{ee}}[L_{es}(\bar{v}_s\Delta p + \Delta\mu_s^c) + L_{ew}(\bar{v}_w\Delta p + \Delta\mu_w^c)] \tag{55}$$

Since the dialysis $\leftrightarrow$ osmosis experiment is performed at uniform pressure, this reduces to

$$\left(\frac{J_s}{-\Delta\mu_s^c}\right)_{\substack{i=0\\ \Delta p=0}} = L_{ss} - \frac{L_{se}L_{es}}{L_{ee}} + \left(L_{sw} - \frac{L_{es}L_{ew}}{L_{ee}}\right)\frac{\Delta\mu_w^c}{\Delta\mu_s^c} \tag{56}$$

*The principal investigator has at his disposal a complete tubular hyperfiltration apparatus in which this salt rejection effect is being measured simultaneous with the hyperfiltration rate and with streaming potentials across modified cellulose acetate membranes at pressures up to 100 atm (19). This apparatus is in use for another project, however, and would have to be modified to provide the data necessary here, and this could not be done in the past.

The determination of L_{ee} and L_{ew} has already been described--see eqs. (40) and (52) respectively. L_{es} could not be determined by experiments, but has been assumed equal to L_{se}[eq. (42)] in view of the reciprocity relation (50). The salt flux, $(J_s)_{i=0,\Delta p=0}$ was determined in the dialysis experiment. Hence the only two unknowns in eq. (56) are L_{ss} and L_{sw}.

In the same manner we obtain from eq. (36) for the water flux:

$$(J_w)_{i=0} = L_{ws}(-\bar{v}_s\Delta p - \Delta\mu_s^c) + L_{ww}(-\bar{v}_w\Delta p - \Delta\mu_w^c) + (L_{we}/L_{ee})(L_{es}\Delta\mu_s^c + L_{es}\bar{v}_s\Delta p + L_{ew}\Delta\mu_w^c + L_{ew}\bar{v}_w\Delta p) \tag{57}$$

Since the pressure is uniform, this reduces to

$$\left(\frac{J_w}{-\Delta\mu_w^c}\right)_{i=0} = L_{ww} - \frac{L_{we}L_{ew}}{L_{ee}} + \left(L_{ws} - \frac{L_{we}L_{es}}{L_{ee}}\right)\frac{\Delta\mu_s^c}{\Delta\mu_w^c} \tag{58}$$

The unknowns in this equation are L_{ww} and L_{ws}*.

To evaluate the hyperfiltration experiment, we divide eq. (57) by $-\Delta p$:

$$\left(\frac{J_w}{-\Delta p}\right)_{i=0} = L_{ws}\bar{v}_s + \frac{\Delta\mu_s^c}{\Delta p} + L_{ww}\bar{v}_w + \frac{\Delta\mu_w^c}{\Delta p} - (L_{we}/L_{ee})(L_{es}\frac{\Delta\mu_s^c}{\Delta p} + L_{es}\bar{v}_s + L_{ew}\frac{\Delta\mu_w^c}{\Delta p} + L_{ew}\bar{v}_w) \tag{59}$$

The water flux, J_w, is measured as a function of the pressure difference, $-\Delta p$. The unknowns in this equation are L_{ws} and L_{ww}.

Thus it is possible to determine the three unknowns L_{ww}, $L_{ws} = L_{sw}$ and L_{ss} by solution of the three equations (56), (58) and (59), provided all

*Note that the method of calculation for L_{we} has already been described [eq. (44)].

experiments were performed under the same concentration gradient.

Our hyperfiltration experiments were performed at conditions of uniform concentration (i.e. $\mu_s^c = 0 = \mu_w^c$; no osmosis) by "clamping" the concentrations of the two solutions adjacent to the membrane at equal concentrations of about 0.1 M KCl. For this case eq. (59) reduces to the simple form

$$\left[J_w/(-\Delta p)\right]_{\substack{i=0 \\ \Delta p=0}} = (L_{ws})_{\Delta\mu=0}\,\bar{v}_s + (L_{ww})_{\Delta\mu=0}\,\bar{v}_w - (L_{we}/L_{ee})_{\Delta\mu=0}\left[(L_{es})_{\Delta\mu=0}\,\bar{v}_s + (L_{ew})_{\Delta\mu=0}\,\bar{v}_w\right] \tag{60}$$

In principle it is not permissible to solve the triplet of equations (56), (57) and (60) for L_{ww}, $L_{ws} = L_{sw}$, and L_{ss}, because the first two equations refer to a dialysis experiment which, by definition requires a concentration gradient, while the last equation refers to an experiment at uniform concentration. In the future, we plan to maintain the finite concentration difference in all experiments (as we have indeed occasionally done in the past), but for the purpose of this report we shall utilize the results of the latest measurements, as presented in Table I, in which the water flux under pressure was measured under conditions of $\Delta\mu=0$. Since L_{ww} is similar to a d'Arcy permeability constant, and since it is known that these "constants" vary but little with concentration (provided the concentration is below about 1 M), we do not think that the value of L_{ww} would have been appreciably different if the concentrations of the solutions in the hyperfiltration experiment had been identical with those in the dialysis $\leftrightarrow$ osmosis experiment*. In fact it

*The water flux, as opposed to the coefficient L_{ww} would change very appreciably, however, since, in addition to the pressure force, the osmotic force would drive the water through the membrane.

is usually tacitly assumed that the conductance coefficient L_{ww} is independent of the concentrations of the solutions bracketing the membrane (1). As for the coefficient $L_{ws} = L_{sw}$, some dependence on the solution concentrations is expected (20), but this dependence is neglected in this report. Consequently, the three coefficients L_{ww}, $L_{ws} = L_{sw}$ and L_{ss} are determined by solution of the simultaneous equations (56), (58) and (60). The calculations are presented in part A. 2. of the Appendix. The results of the calculations of all conductance coefficients in the M-K matrix are presented in Table 4.

Conclusions

While it is not easy to draw immediate conclusions on the transport mechanism from the phenomenological conductance coefficients, L^*, several important points emerge from consideration of the L-values in Table 4 and the methods used to calculate these values:

First, the coefficients related to a larger extent to the solvent than to the salt are larger ($L_{ew} >> L_{es}$; $L_{ww} >> L_{ws}$; $L_{sw} >> L_{ss}$). This is probably due to the much higher concentration of water than of salt in the ion-exchange membrane, for the coefficients L_{ij} increase in general with increasing c_j [while the flux equations in ref. (8) are not identical with equations (35)-(37) used here, some insight into the physical meaning of the L-coefficients, and in particular the above conclusion about their

---

*On the other hand, friction coefficients, which can be calculated from the complete group of L-coefficients are useful for this purpose (8-10). We plan to perform such calculations in the future. We expect that it will be useful to invert the flux-force equations first, i.e. present the forces as sums of terms linear with respect to the fluxes, and calculate the friction coefficients from the resulting resistance coefficients, R_{ij}(2).

TABLE 4

Phenomenological Coefficients for System 0.05 N NaCl | C-103* | 0.1 N NaCl

These conductivity coefficients, L, refer to the flux equations (35)-(37). All coefficients have the units joule^{-1} mole^{2} cm^{-2} sec^{-1}**.

L_{ee}	1.89×10^{-11}***	
L_{se}	1.64×10^{-11}***	L_{es} assumed equal to L_{se}
L_{we}	1.88×10^{-10}***	reciprocal pair
L_{ew}	1.77×10^{-10}***	reciprocal pair
L_{ws}	1.73×10^{-10}	L_{sw} assumed equal to L_{ws}
L_{ss}	1.42×10^{-11}	
L_{ww}	1.31×10^{-8}	

---

* Cation-exchange membrane made by American Machine and Foundry Company, Stamford, Connecticut.

** 1 joule = 1 wattsec = 1 dekabar cm^{3}.

*** Determined from measurements on system without concentration gradient, 0.1 N NaCl | C-103 | 0.1 N NaCl.

variation with c_j (borne out by the results) may be obtained from that reference; see eqs. (17) or (32) of reference (8)]. This property of the set of L-coefficients thus probably reflects the exclusion of salt from the ion-exchange membrane ("Donnan effect").

Second, one of the three reciprocity relations was tested by the results of our experiments, and was confirmed within about six percent for the conditions used in these measurements.

Third, the numerical calculations in section A. 2. of the Appendix show the large dependence of all L-coefficients on the membrane conductance (Figure 4). In fact, membrane conductance emerges as the most decisive transport characteristic, thus justifying a posteriori the time-honored decision of battery technologists to use conductance measurements as primary screening tests for separator materials. The implication of this conclusion for future experiments is the emphasis on refinements of the technique of membrane conductance measurements. A more elaborate and more accurate technique than the one used in the past is being developed. It uses the existing apparatus described in Progress Report No. 12. Apparatus and procedure were modified to yield much more accurate measurements of the distances of the electrodes from the membrane. In case future measurements yield a somewhat different conductance value, all L-coefficients in Table 4 will be different, but their ratios will not change much.

Fourth, consideration of the numerical values of all terms in the calculation of the conductance parameter, L_{ss}, which relates the rate of electrolyte diffusion through the membrane to the "electrolyte diffusion force", $-\Delta\mu_s$, (determined by the concentration gradient of the electrolyte)

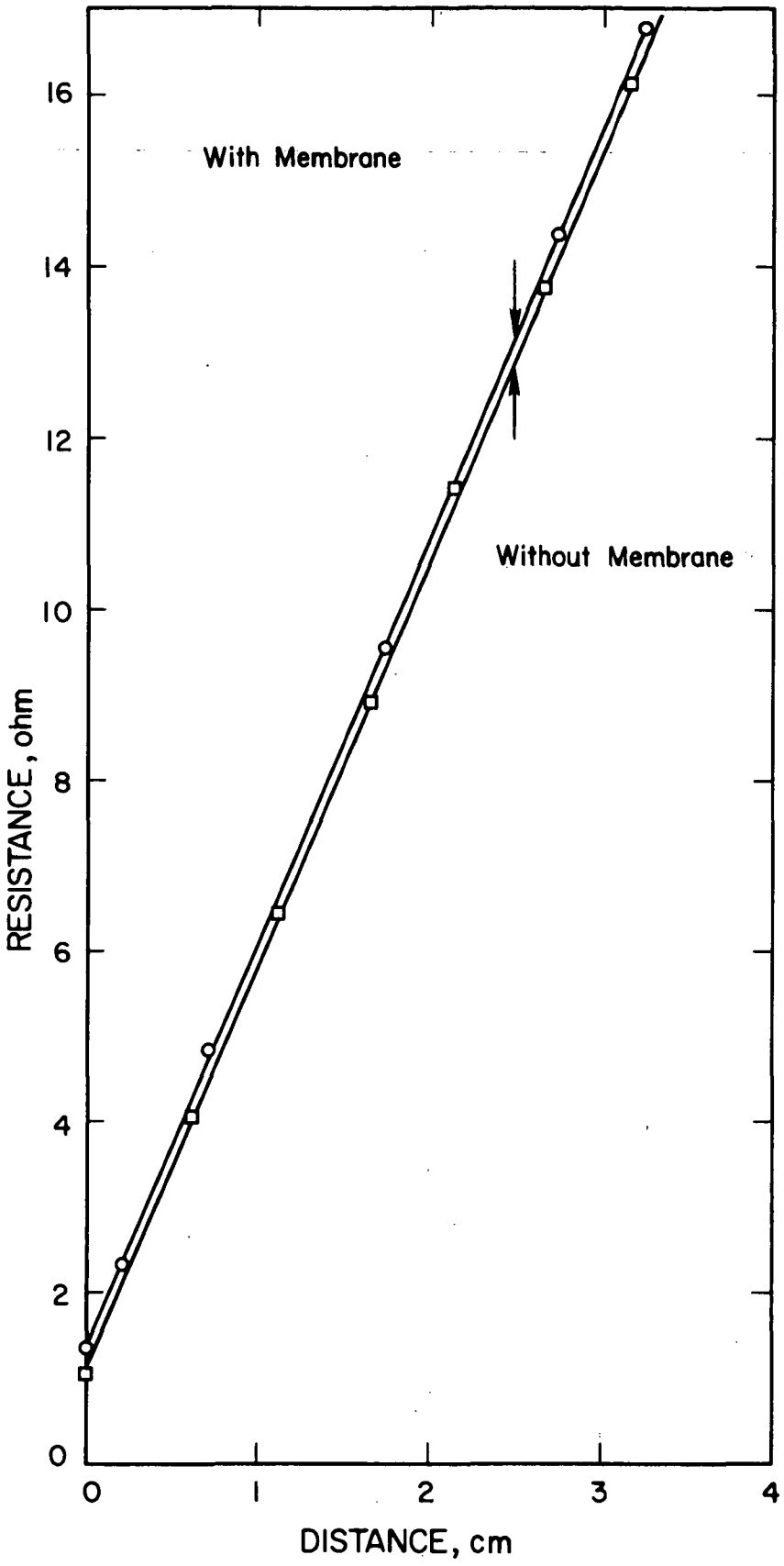

FIGURE 4. C-103 Membrane. Evaluation of Resistance (25°C).

Solution 0.1 N NaCl. Active area = 20.25 cm^2. Abscissa represents distance from point of closest approach of electrodes to membrane (upper line) or electrode distance (lower line). Resistance of membrane is determined from ordinate distance of the two parallel lines. For lower line ordinate intercept represents circuit impedance.

leads one to the conclusion that osmosis $\leftrightarrow$ dialysis with shorted electrodes (rather than with unconnected electrodes) should be tried, in an attempt to improve the accuracy of this determination. Also it would be worthwhile to investigate under what conditions, if any, the planned, simultaneous application of several independent forces improves the accuracy of the determination of the conductance coefficients, L.

Finally, the methods developed here for calculating a set of L-coefficients from specified transport measurements lead to the unequivocal characterization of any system of the type: solution | membrane | solution, provided only that these specified measurements can be performed with sufficient accuracy. The "concentration-clamp" apparatus developed in this project represents a large step towards the attainment of this experimental aim; the following next steps are desirable: (a) further refinements of the apparatus and procedure in order to obtain this desired accuracy in a few types of transport measurements in which we still need these improvements, and (b) the systematic collection of transport data.

Acknowledgement

The Principal Investigator and his collaborators thank Mrs. J. Worthington for her valuable editorial help.

APPENDIX

A. 1. Relation of electrical potential difference, $\Delta\phi$, across the membrane, to potential difference, $\Delta\phi_-$, between two Ag/AgCl electrodes.

Consider the isothermal system

$$\text{Ag/AgCl} \;\big|\; \text{NaCl solution, c', p'} \;\big|\; \text{Membrane} \;\big|\; \text{NaCl solution, c", p"} \;\big|\; \text{Ag/AgCl}$$

The condition for equilibrium between each solution and the Ag/AgCl electrode in contact with it is that the sum of the total potentials* of the reactants equals that of the products. The electrochemical electrode equilibrium is

$$Ag + Cl^- \rightleftharpoons AgCl + e^- \qquad \text{(A1-4)}$$

where e^- stands for one mole of electrons in the silver metal. Thus the equilibrium conditions for the two electrodes respectively are

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*The total potential of component i, $\tilde{\mu}_i$, is the sum of the contributions of the pressure-dependent, concentration-dependent, and electric field-dependent parts of the (chemical) potential (12, p. 94, 469, 480)

$$\tilde{\mu}_i = \mu_i^0 + (p - 0.1013)\,\bar{v}_i + \underbrace{RT\ln a_i}_{\mu_i^c - \mu_i^0} + z_i \mathcal{F}\phi \qquad \text{(A1-1)}$$

where $\tilde{\mu}_i^0$ is the standard potential, z_i the valency of the particle (+1 for Ag^+, -1 for Cl^-, zero for species carrying no appreciable net charge, e.g. Ag and AgCl) and ϕ the electrical potential (volt) at the locations considered:

$$\tilde{\mu}_{AgCl} = \mu_{AgCl}^c + (p - 0.1013)\,\bar{v}_{AgCl} \equiv \mu_{AgCl} \qquad \text{(A1-2)}$$

and similarly for silver:

$$\tilde{\mu}_{Ag} = \mu_{Ag} \qquad \text{(A1-3)}$$

Note that the pressure is measured in dekabar (0.1013 dekabar = 1 atm).

$$\mu''_{Ag} + \tilde{\mu}''_{Cl^-} = \mu''_{AgCl} + \tilde{\mu}''_{e^-} \qquad \text{(A1-5)}$$

$$\mu'_{Ag} + \tilde{\mu}'_{Cl^-} = \mu'_{AgCl} + \tilde{\mu}_{e^-} \qquad \text{(A1-6)}$$

Subtract (A1-6) from (A1-5)

$$\Delta\mu_{Ag} + \Delta\tilde{\mu}_{Cl^-} = \Delta\mu_{AgCl} + \Delta\tilde{\mu}_{e^-} \qquad \text{(A1-7)}$$

Because of the small volume of the (non-hydrated) electrons, the effect of pressure on the total potential of the electrons is assumed to be negligible. Also, since the electron concentration in the wire, and hence $\mu^c_{e^-}$, are nearly uniform, it follows from (A1-1) that

$$\Delta\tilde{\mu}_{e^-} \; (\equiv \Delta\mu_{e^-} - \mathcal{F}\Delta\phi_-) \simeq -\mathcal{F}\Delta\phi_- \qquad \text{(A1-8)}$$

where $\Delta\phi_-$ is the electrical potential difference between the electrodes.

Substitute for $\Delta\tilde{\mu}_{e^-}$ in eq. (A1-8) from (A1-7)

$$\Delta\tilde{\mu}_{e^-} = -\mathcal{F}\Delta\phi_- = \Delta\tilde{\mu}_{Cl^-} - (\Delta\mu_{AgCl} - \Delta\mu_{Ag}) \qquad \text{(A1-9)}$$

According to "Poynting's equation" (12, p. 304), the variation with pressure of the free energy of one mole, G_i/n_i of a pure component i, is related to the total volume, V_i, of n_i mole of this component by:

$$\left(\frac{\partial G/n_i}{\partial p}\right)_T = V_i/n_i \qquad \text{(A1-10)}$$

Applying (A1-10) to pure AgCl and Ag respectively, we obtain:

$$\Delta(G_{AgCl}/n_{AgCl})_T = \Delta\mu_{AgCl} = \bar{v}_{AgCl}\,\Delta p \qquad \text{(A1-11)}$$

$$\Delta(G_{Ag}/n_{Ag})_T = \Delta\mu_{Ag} = \bar{v}_{Ag}\,\Delta p \qquad \text{(A1-12)}$$

Here we have used the fact that, by definition of the partial molar quantities, the molar free energies, G_i/n_i and the molar volumes V_i/n_i of pure substances are identical with the partial molar free energies, μ_i, (chemical potentials) and partial molar volumes, $\bar{v}_i$, respectively.

Substituting $\Delta\mu_{AgCl}$ and $\Delta\mu_{Ag}$ from (A1-11) and (A1-12) respectively in (A1-9), we obtain

$$\Delta\mu_{e^-} = -\mathcal{F}\Delta\phi_- = \Delta\tilde{\mu}_{Cl^-} - \Delta p(\bar{v}_{AgCl} - \bar{v}_{Ag}) \qquad \text{(A1-13)}$$

Therefore the potential difference, $\Delta\phi_-$, between the two Ag/AgCl electrodes is

$$\Delta\phi_- = -(1/\mathcal{F})[\Delta\tilde{\mu}_{Cl^-} - \Delta p(\bar{v}_{AgCl} - \bar{v}_{Ag})] = -(1/\mathcal{F})[\Delta\tilde{\mu}_- - \Delta p v_{Cl}] \qquad \text{(A1-14)}$$

where the symbol v_{Cl} replaces $(\bar{v}_{AgCl} - \bar{v}_{Ag})$ and symbol $\tilde{\mu}_-$ replaces $\tilde{\mu}_{Cl^-}$, for the sake of brevity.

Comparison of this result with equation (12-6) p. 150 of ref. (2) shows that in the latter, the term $\Delta p(\bar{v}_{AgCl} - \bar{v}_{Ag})$ has been neglected.

Let us examine to which extent this term affects the evaluation of the results of our experiments. To do so, we calculate first the numerical magnitude of the expression $\Delta p(\bar{v}_{AgCl} - \bar{v}_{Ag})$:

From ref. (13), p. 648, the specific gravity and molecular weight of silver are 10.5 g cm^{-3} and 107.88 respectively. Hence

$$\bar{v}_{Ag} = \frac{107.88 \text{ g mole}^{-1}}{10.5 \text{ g cm}^{-3}} = 10.28 \text{ cm}^3 \text{ mole}^{-1}$$

and, from the same source $\bar{v}_{AgCl} = \frac{143.34}{5.56} = 25.8\ cm^3\ mole^{-1}$

Hence $-\frac{1}{\mathcal{F}} \Delta p(\underbrace{\bar{v}_{AgCl} - \bar{v}_{Ag}}_{v_{Cl^-}})$

$$= -\frac{1}{0.965 \times 10^5\ amp\ sec\ eq^{-1}} \underbrace{(25.8 - 10.28)}_{\sim 15.5}\ cm^3\ mole^{-1}\ \Delta p$$

$$= -1.61 \times 10^{-4}\ \frac{cm^3}{amp\ sec}\ \Delta p$$

For $\Delta p = -0.2$ dekabar (about 2 atm) this yields

$$-\frac{1}{\mathcal{F}}(\bar{v}_{AgCl} - \bar{v}_{Ag})\Delta p = 1.61 \times 10^{-4} \times 0.2\ \frac{cm^3\ dekabar}{amp\ sec} = 3.22 \times 10^{-5}\ volt$$

i.e. -0.032 millivolt for 2 dekabar.

The streaming potential for the C-103 membrane considered in this report was more than one order of magnitude higher. We conclude that as a very first approximation, eq. (12-6) of ref. (2) may be used, but that the correction term $\Delta p(\bar{v}_{AgCl} - \bar{v}_{Ag})$ is not entirely negligible.

Returning to eq. (A1-14), we substitute for $\Delta\mu_{Cl^-}$ in terms of the definition of the total potential [eq. (A1-1)]:

$$\Delta\phi_- = -(1/\mathcal{F})[\Delta\mu^c_{Cl^-} + \bar{v}_{Cl^-}\Delta p - \mathcal{F}\Delta\phi - \Delta p(\bar{v}_{AgCl} - \bar{v}_{Ag})]$$

$$= -(1/\mathcal{F})[\Delta\mu^c_{Cl^-} - \mathcal{F}\Delta\phi - \Delta p(\bar{v}_{AgCl} - \bar{v}_{Ag} - \bar{v}_{Cl^-})] \qquad (A1\text{-}15)$$

Now, if the volume change in the electrochemical reactions at the electrodes [eq. (A1-4)] is negligible, then the last term of equation (A1-15) is negligible (15b).*

Therefore:

$$\Delta\phi_{-} \simeq -(\Delta\mu^{c}_{Cl^-}/\mathcal{F}) + \Delta\phi \qquad \text{(A1-16)}$$

One can calculate the potential drop across the membrane, $\Delta\phi$, which represents the difference in electrical potential between the two solutions in the immediate vicinity of the membrane surfaces, by simply adding a "concentration correction", $(\Delta\mu^{c}_{Cl^-}/\mathcal{F}) = (RT/\mathcal{F})\ln(a''_{Cl^-}/a'_{Cl^-})$ to the potential difference, $\Delta\phi_{-}$, measured between the Ag/AgCl electrodes:

$$\Delta\phi \simeq \Delta\phi_{-} + (\Delta\mu^{c}_{Cl^-}/\mathcal{F}) \qquad \text{(A1-17)}$$

$\Delta\phi$ appears as a component of the general driving force of the Onsager set of flux equations (3)-(5). Note that eq. (A1-17) was presented (without proof) in the 1968 Annual Progress Report.

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*Note that this term is likely to be much smaller than the term $\Delta p(\bar{v}_{AgCl} - \bar{v}_{Ag})$ discussed in connection with eq. (A1-14).

A. 2. Calculation of M-K Conductivity Coefficients, L

All experimental values used are from Table 3.

$$L_{ee} = \frac{\kappa}{d}/\mathcal{F}^2 = \frac{1}{\rho d \mathcal{F}^2}$$

$$R = \frac{\rho d}{A} \longrightarrow \rho d = RA$$

$R = 0.28$ ohm (from Figure 4)

$RA = 0.28\ \Omega \times 20.25\ cm^2 = 5.67$ ohm cm^2

$$\rho = \frac{\rho d}{d} = \frac{5.67}{0.017} = 332 \text{ ohm cm}$$

$$\kappa = 1/\rho = 3.01 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$(L_{ee})_{\Delta\mu=0} = 1/(\rho d \mathcal{F}^2) = 1/(5.67 \times 0.965^2 \times 10^{10}) = \underline{1.89 \times 10^{-11} \text{ joule}^{-1} \text{eq}^2 \text{sec}^{-1} \text{cm}^{-2}}$$

L_{se} [from eq. (42)]

$$(L_{se})_{\Delta\mu=0} = t_+ L_{ee}$$

where

$$t_+ \equiv \left(\frac{J_s}{i/\mathcal{F}}\right)_{\Delta\mu=0} = \frac{-8.69 \times 10^{-9} \text{ mole cm}^{-2} \text{ sec}^{-1} \times 0.965 \times 10^5 \text{ coul eq}^{-1}}{-0.971 \times 10^{-3} \text{ amp cm}^{-2}} = 0.864$$

$$\underline{(L_{se})_{\Delta\mu=0}} = t_+ L_{ee} = \underline{1.64 \times 10^{-11} \text{ eq}^2 \text{ joule}^{-1} \text{ sec}^{-1} \text{ cm}^{-2}}$$

L_{we}

From eq. (44) $\quad (L_{we})_{\Delta\mu=0} = t_w (L_{ee})_{\Delta\mu=0}$

where

$$t_w \equiv [J_w/(i\mathcal{F})]_{\Delta\mu=0} = \frac{-99.79 \times 10^{-9} \text{ mole cm}^{-2} \text{ sec}^{-1} \times 0.965 \times 10^{5} \text{ coul eq}^{-1}}{0.971 \times 10^{-3} \text{ amp cm}^{-2}} = 9.92$$

$$\underline{(L_{we})_{\Delta\mu=0}} = t_w L_{ee} = 9.92 \times 1.89 \times 10^{-11} = \underline{1.88 \times 10^{-10} \text{ joule}^{-1} \text{ eq}^{2} \text{ sec}^{-1} \text{ cm}^{-2}}$$

$\underline{L_{ew}}$

From eq. (52):

$$(L_{ew})_{\Delta\mu=0} = \frac{1}{\bar{v}_w}\left[\mathcal{F} L_{ee}\left(\text{SPD} + \frac{v_{Cl}}{\mathcal{F}}\right) - L_{se}\bar{v}_s\right]$$

From streaming-potential line, $\text{SPD} = 0.176 \times 10^{-3} \frac{\text{volt}}{\text{atm}} \times 9.87 \frac{\text{atm}}{\text{dekabar}^*}$

$$\text{SPD} = 1.737 \times 10^{-3} \text{ volt dekabar}^{-1}$$

$$(L_{ew})_{\Delta\mu=0} = \frac{1}{18.02} \text{ moles cm}^{-3} \Big[0.965 \times 10^{5} \text{ coul mole}^{-1} \times 1.89 \times 10^{-11} \text{ joule}^{-1}\text{eq}^{2}\text{sec}^{-1}\text{cm}^{-2} \Big(\overbrace{1.737 \times 10^{-3}}^{1.898 \times 10^{-3}} \text{ volt dekabar}^{-1} + \frac{15.5 \text{ cm}^3\text{mole}^{-1}**}{0.965 \times 10^{5}\text{coul mole}^{-1}}\Big) - 1.64 \times 10^{-11} \text{ eq}^{2}\text{joule}^{-1}\text{sec}^{-1}\text{cm}^{-2} \times 17.2 \text{ cm}^3 \text{ mole}^{-1}***\Big]$$

$$\underline{(L_{ew})_{\Delta\mu=0}} = \frac{1}{18.02}[348 \times 10^{-11} - 28.2 \times 10^{-11}] = \underline{1.77 \times 10^{-10} \text{ joule}^{-1}\text{mole}^{2}\text{cm}^{-2}\text{sec}^{-1}}$$

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* 1 dekabar ≡ 10 bar = 9.8 atm. This unit was introduced (8) because it eliminates conversion factors when all electrical and osmotic measurements are expressed in units containing the practical wattsec = joule (1).

** From appendix A.1.

*** Ref. 21, p. 250, eq. (8-5-4). Parameters for equation from p. 253, Table 8-5-1.

L_{ww}, $L_{ws} = L_{sw}$ and L_{ss}

To calculate these coefficients (all at $\Delta\mu \neq 0$), we first calculate $\Delta\mu_s^c$ and $\Delta\mu_w^c$.

$c_s'' = 1.001_6 \times 10^{-4}$ mole cm^{-3} $(= 0.1001_6 N)$

$c_s' = 0.495_4 \times 10^{-4}$ mole cm^{-3} $(= 0.0495_4 N)$

The mean activity coefficients, $\gamma_\pm$, of Na^+ (or Cl^-) are obtained by interpolation from ref. (22, Appendix 8.9, p. 466*). Since the solutions are rather dilute, ratios of molar concentrations are sometimes substituted for ratios of molality throughout the following calculations:

$c' = 0.0495 \times 10^{-3}$ mole cm^{-3} $(m' = 0.0497$ mole NaCl/1000 g H_2O, $\sqrt{m} \approx 0.223)$; $\gamma_\pm' = 0.821$

$c'' = 0.1001 \times 10^{-3}$ mole cm^{-3} $(m'' = 0.1005$ mole NaCl/1000 g H_2O, $\sqrt{m} \approx 0.317)$; $\gamma_\pm'' = 0.780$

$$\left(a_s'/a_s''\right)_\pm = c'\gamma_\pm'/(c''\gamma_\pm'') = (0.0497 \times 0.821)/(0.1006 \times 0.780) = 0.52$$

$$\underline{\Delta\mu_s^c} = RT\ln(a_\pm''/a_\pm')^2 = 2 \times 8.13 \text{ joule mole}^{-1}(^oK)^{-1} \times 298(^oK)[\underbrace{-\ln(0.52)}_{0.65393}] = \underline{3169 \text{ joule mole}^{-1}}$$

The water activities are found by linear interpolation of published data (ref. 22, Appendix 8.3).

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*Comparison with other references showed that the term "activity coefficient of electrolyte" used in the heading of this table stands for the mean activity coefficient, $\gamma_\pm$, of the Na^+ ions (equal to the mean activity coefficient of the Cl^- ions). The activity coefficient of the salt, γ_{NaCl}, equals $\gamma_\pm^2$ (14, Table 1).

m = 0.0497 mole NaCl/1000 g H_2O: $a_w' = 0.998332$

m = 0.1006 mole NaCl/1000 g H_2O: $a_w'' = 0.996626$

$$\Delta\mu_w^c = RT\ln(a_w''/a_w') \simeq RT\ln(\Delta a_w/\bar{a}_w)$$

$$= -8.13 \text{ joule mole}^{-1}(\text{deg K})^{-1} \times 298\ ^oK \times (0.001706/0.997)$$

$$\Delta\mu_w^c = -4.15 \text{ joule mole}^{-1}*$$

We wish to substitute numerical values in eq. (58). From Table 3, the dialysis $\leftrightarrow$ osmosis experiment 145, yielded the following flux-force ratio:

$$\left(\frac{J_w}{-\Delta\mu_w^c}\right)_{\substack{i=0 \\ \Delta p=0}} = \frac{15.3 \times 10^{-9} \text{ mole cm}^{-2} \text{ sec}^{-1}}{4.15 \text{ joule mole}^{-1}} = 3.7 \times 10^{-9} \text{ joule}^{-1} \text{ mole}^2 \text{ cm}^{-2} \text{ sec}^{-1}$$

*It is of interest to compare the ratio $\Delta\mu_s^c/\Delta\mu_w^c$ to the corresponding value calculated from the Gibbs-Duhem equation [eq. (9)]. We obtained $(\Delta\mu_s^c/\Delta\mu_w^c) = 3169/(-4.15) = -764$, whereas the Gibbs-Duhem equation yields $-\bar{c}_s/\bar{c}_w = -55.5/0.075 = -740$. The discrepancy is due to the fact that, strictly, the Gibbs-Duhem equation is applicable only to very small concentration differences, dc. When used for finite concentration differences, $c_s'' - c_s'$, proper integration has to be performed, instead of using simply the average salt concentration, $\bar{c}_s$.

Substituting this experimental value in eq. (58) and taking L_{es} as equal to L_{se}, we obtain

$$3.7 \times 10^{-9} = L_{ww} - \underbrace{\frac{1.88 \times 10^{-10} \times 7.77 \times 10^{-10}}{1.89 \times 10^{-11}}}_{1.76 \times 10^{-9}} + \left(L_{ws} - \underbrace{\frac{1.88 \times 10^{-10} \times 1.64 \times 10^{-11}}{1.89 \times 10^{-11}}}_{1.627 \times 10^{-10}} \right) \underbrace{\frac{3170}{(-4.15)}}_{-764}$$

$$\underbrace{(3.7 + 1.76) \times 10^{-9} - 124.6 \times 10^{-9}}_{-119.1 \times 10^{-9}} = L_{ww} - 764\, L_{ws}$$

Another relation between L_{ww} and L_{ws} is obtained from eq. (59). From Table 3, we obtain the following hydraulic permeability values:

$$\left(\frac{J_v}{-\Delta p} \right)_{i=0} = \frac{0.374 \times 10^{-6} \text{ cm sec}^{-1}}{1 \text{ atm}} \times 9.87 \text{ atm dekabar}^{-1} = 3.69 \times 10^{-6} \text{ cm dekabar}^{-1}\text{sec}^{-1}$$

and $\quad \frac{0.304}{0.8} \times 9.87 \qquad \underline{3.75 \times 10^{-6} \text{ cm dekabar}^{-1}\text{sec}^{-1}}$

Average $\quad 3.72 \times 10^{-6} \text{ cm dekabar}^{-1}\text{sec}^{-1}$

The hyperfiltration effect was too small to be measured. Hence we take the composition of the permeate equal to that of the solution

$$J_s/J_w = c_s/c_w = 10^{-4} \text{ mole cm}^{-3}/55.5 \times 10^{-3} \text{ mole cm}^{-3} = 1.8 \times 10^{-3}$$

$$J_v = J_w \bar{v}_w + J_s \bar{v}_s = J_w [\bar{v}_w + 1.8 \times 10^{-3}\, \bar{v}_s]$$

Take $\bar{v}_w = 18.02\ cm^3\ mole^{-1}$ [calculated from eq. (13.60), ref. (23)]

$\bar{v}_s = 17.49\ cm^3\ mole^{-1}$ [calculated from eq. (13.54), ref. (23)]

Then $J_v = 18.05\ J_w$

and

$$\left(\frac{J_w}{-\Delta p}\right)_{\substack{i=0 \\ \Delta\mu=0}} = \frac{1}{18.05}\left(\frac{J_v}{-\Delta p}\right)_{i=0} = \frac{1}{18.05\ cm^3\ mole^{-1}} \times 3.72 \times 10^{-6}\ cm\ dekabar^{-1}\ sec^{-1}$$

$$\left(\frac{J_w}{-\Delta p}\right)_{i=0} = 2.06 \times 10^{-7}\ mole\ dekabar^{-1}\ cm^{-2}\ sec^{-1}$$

Substitute this value in eq. (59), simplified because $\Delta\mu_w = 0 = \Delta\mu_s$

$$2.06 \times 10^{-7} = 17.2\ L_{ws} + 18.02\ L_{ww} - \frac{1.88 \times 10^{-10}}{1.90 \times 10^{-11}}\ \underbrace{(1.64 \times 10^{-11} \times 17.2 + 1.77 \times 10^{-10} \times 18.02)}_{3.48 \times 10^{-9}}$$

$$\underbrace{2.06 \times 10^{-7} + 3.46 \times 10^{-8}}_{2.41 \times 10^{-7}} = 18.02\ L_{ww} + 17.49\ L_{ws}$$

Rewriting the two simultaneous equations for L_{ww} and L_{ws}, we have:

$$L_{ww} - 764\ L_{ws} = -1.191 \times 10^{-7}$$

$$L_{ww} + 0.971\ L_{ws} = 1.33 \times 10^{-8}$$

$$765\ L_{ws} = 1.324 \times 10^{-7} \rightarrow \underline{L_{ws}(=L_{sw}) = 1.73 \times 10^{-10}\ joule^{-1} mole^2 cm^{-2} sec^{-1}}$$

$$L_{ww} = 1.33 \times 10^{-8} - 0.017 \times 10^{-8} = \underline{1.31 \times 10^{-8}\ joule^{-1} mole^2 cm^{-2} sec^{-1}}$$

L_{ss} is calculated from eq. (56) as follows:

From Table 3 we obtain for the salt permeability coefficient

$$\left(\frac{J_s}{-\Delta\mu_s}\right)_{\substack{i=0 \\ \Delta p=0}} = \frac{-0.0713 \times 10^{-9} \text{ mole cm}^{-2} \text{ sec}^{-1}}{-3170 \text{ joule mole}^{-1}} = 2.25 \times 10^{-14} \text{ joule}^{-1}\text{mole}^2\text{cm}^{-2}\text{sec}^{-1}$$

Substitute this in eq. (56):

$$2.26 \times 10^{-14} = L_{ss} - \frac{(1.64 \times 10^{-11})^2}{1.89 \times 10^{-11}} + 1.73 \times 10^{-10} - \underbrace{\frac{(1.64 \times 10^{-11}) \times 1.77 \times 10^{-10}}{1.89 \times 10^{-11}}}_{1.53 \times 10^{-10}} \left(\frac{-4.15}{3169}\right)$$

$$2.26 \times 10^{-14} = L_{ss} - 1.423 \times 10^{-11} + 2.54 \times 10^{-14}$$

It is seen that the dominant term in this equation is $(L_{se}L_{es}/L_{ee}) = 1.415 \times 10^{-11}$. In other words, relatively large errors in the salt diffusion flux, J_s, which determines the first term on the left, 2.26×10^{-14}, affect the value calculated for L_{ss} relatively little; the salt flux is primarily determined by the presence of an electrical potential difference across the membrane, rather than the "diffusion force", $-\Delta\mu_s^c$.*

From the last equation

$L_{ss} = 1.423 \times 10^{-11}$ joule^{-1} mole^2 cm^{-2} sec^{-1}

Table 4 in the main body of this report is a summary of the M-K conductivity coefficients, L, calculated in this appendix.

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*If it were possible to effectively short the electrodes during the dialysis $\leftrightarrow$ osmosis experiment ($\Delta\phi_- = 0$), one could calculate L_{ss} by substituting the salt flux measured under these conditions into eq. (35),

*and thus eliminate this difficulty, because the resulting equation no longer contains the large term $(L_{se}L_{es}/L_{ee})$

$$(J_s)_{\substack{\Delta\phi=0 \\ \Delta p=0}} = L_{ss}(-\Delta\mu_s) + L_{sw}(-\Delta\mu_w)$$

It should be noted, however, that in this case the electrodes would have to be placed very close to the membrane faces, since the results of this measurement are expected to vary substantially with the distance of the electrodes from the membrane. As discussed in the introductory part of the section "Method for calculation of the L-conductance coefficients for the M-K transport equations", all the L-coefficients are to reflect membrane properties rather than solution properties. Therefore the method of evaluation was developed by a reasoning involving a thought experiment in which the electrodes are brought infinitely close to the membrane surfaces. It was shown that many transport measurements in which this condition is not met may be substituted, however, without materially affecting the results. The exceptions to this rule are the measurement of the electrical resistance (in which the resistance for the conditions prevailing in the thought experiment was readily found, however, by extrapolating the straight-line plot of resistance vs. electrode distance to the distance corresponding to the electrodes touching the membrane faces), and the measurement discussed in this footnote. Here, too, a suitable extrapolation method might prove applicable in the future;in this case the current through the electrode "short" has to be measured.

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